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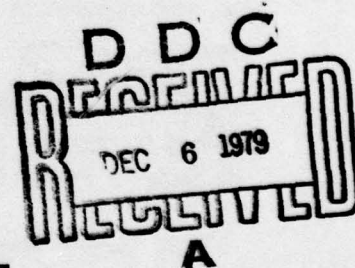NATIONAL BUREAU OF STANDARDS-1963-A

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CALCIUM INORGANIC ELECTROLYTE BATTERY DEVELOPMENT

R. HIGGINS & L. ELLIOTT

EAGLE-PICHER INDUSTRIES INCORPORATED
ELECTRONICS DIVISION
JOPLIN, MISSOURI 64801

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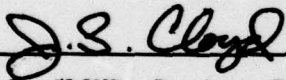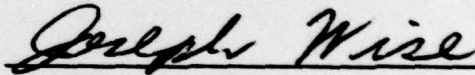WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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The objectives of this program are based on the desire to develop a calcium/oxyhalide system comparable to the lithium/oxyhalide system with respect to energy density and rate capabilities, while overcoming the problems of voltage delay and safety hazards. This project is directed toward assessing basic performance, safety, storage, and voltage delay of the calcium/oxyhalide system for use in Air Force applications. Early small cell development is designed for use in life support, rescue equipment, and spacecraft power, while

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→ Phase II development of large cells up to 10,000 Ampere hours is
anticipated for use in missile standby and emergency ground power
systems. Specific factors of concern in these applications are low
volume, performance over a temperature range -40°F to 165°F, safety,
and long shelf life. ←

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SECTION I

INTRODUCTION

During the past ten (10) years, various lithium anode systems have
been developed to fill the need for long shelf life high energy density
batteries, one of which has been $Li/SOCl_2$. Although $Li/SOCl_2$ has exhibited
the highest energy density of all the lithium systems, it has also exper-
ienced the greatest safety problems. In an effort to develop a battery
which retains the high energy density of lithium systems but with increased
safety, a system has been investigated which is composed of the carbon
collector and electrolyte/depolarizer of the $Li/SOCl_2$ but with an anode
of pure calcium. The system is to be evaluated with respect to three (3)
Air Force applications: small cells of less than five ampere hours for life
support equipment; 600 ampere hour cells for space craft power; and 10,000
ampere hour cells for missile standby and emergency ground power systems.

The program is divided into two (2) major phases each lasting eighteen
(18) months. The objective of Phase I was to begin preliminary development
of the system using small hermetically sealed cells. The development to
consist of:

Preliminary investigation

Life support cell design

Storage life evaluation

Safety evaluation.

Preliminary investigation covered evaluation of all materials, mod-
ification of cathode substrate for use with the Ca electrode, development
of the Ca electrode, and design of a sealed cell as a test vehicle for the
system. Immediately following the preliminary investigation was the Life
Support design consisting of design and development of a "half-D" cell for

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life support applications along with basic characterization of the cell from -40°C to 70°C at currents ranging from .05 amp to 1.0 amp. Following design of the "half-D" cell, a storage test was begun to run for eighteen (18) months at room temperature and 55°C. The test utilized approximately one hundred (100) cells with samples removed on monthly schedule. An additional one hundred (100) cells were used to demonstrate safety under a variety of abuse tests.

Phase II of the program will cover design and test of 600 AH to 10,000 AH cells, along with further development in problem areas encountered during Phase I. Phase II efforts will consist of:

Cell performance improvement

Theoretical analysis-cell reaction products and kinetics

600 AH cell development

2000 AH cell development

10,000 AH cell development

Deactivation/Disposal study

Cell performance improvement will cover further development of cell and electrode materials and any other problem areas which might surface during the first phase. The theoretical analysis will be an investigation of the basic cell reaction products as well as the electrode kinetics of the anode. Concurrently with these efforts, a scale up development of the small cell will be conducted to produce a 600 AH cell for evaluation of abuse hazards and as a design aid to further development of larger cells. After evaluation of 600AH cells, 2000 AH cells will be made and tested in demountable cell cases such that the cells can easily be dismantled for examination after discharge. A 10,000 AH cell will be made immediately following analysis of the 2000 AH cells. The 10,000 AH cells will be evaluated during steady

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state discharge, and a variety of abuse tests including reversal short circuit and puncture.

The last effort in Phase II will be a study into the methods of deactivation and disposal of $Ca/SOCl_2$ cells, with particular emphasis on 10,000 AH cells and the safe handling procedures for such cells before, during and after use.

SECTION II

CELL DEVELOPMENT

The approach to the first phase of this program involved applying the current technology of inorganic depolarizers to calcium anodes in an effort to develop a calcium/inorganic system of high energy density capable of meeting the performance requirements of next generation life support, space and standby missile applications. The resulting battery system ideally would have these capabilities without the safety problems currently associated with exisiting high energy systems.

One of the objectives of Phase I was to design and optimize a test vehicle with which to define the parameters of the calcium/inorganic system. The initial investigation was to establish a baseline capability that would determine the extent to which the problems of the lithium/thionyl chloride system would apply to calcium/thionyl chloride, as well as bring to light any unforseen problems unique to the calcium system. The advanced cell development in Phase II will be predicated upon the evaluation of baseline performance in this first phase. Several test vehicles were utilized in these investigations to characterize the system with respect to efficiency of cell structures, cell voltage/current parameters at various temperatures, and effects of material purity and compatibility on performance. Later sealed cells were used to evaluate the calcium/thionyl chloride systems

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sensitivity to fire, detonation or other hazardous conditions resulting from test procedures. Finally, these investigations were to bring out and define any unforseen problems unique to the calcium/thionyl chloride system with subsequent cell design iteration to follow. The first quarter of Phase I was devoted primarily to the discharge of open laboratory-type bag cells, the advantage of these cells being that changes in cathode and anode structure could be quickly instituted and evaluated. This type of construction also allowed for simple access to these structures for examination immediately after discharge. Construction of the test cells utilized a small cathode and anode of 5.0 square centimeters with 0.125 nickel tab current collector spot welded on each electrode and an envelope wrap of glass separator (Dexter or Reeve Angel) surrounding the cathode. Once assembled, the cell materials were carefully inserted in a polyethylene or polypropylene bag with a heat sealed closure. A pair of plexiglas plates were used as support around the bag. Once sealed and in the support plates, electrolyte was added using a syringe and needle. This type of cell was used extensively to evaluate cathode yield, various types of double anodes, carbon black, variation in anode and cathode thickness, and alterations in the electrolyte. Each of these is described under its respective heading.

After evaluation of the basic parameters of the system using bag cells, the first wound sealed cells were made using a "half-D" configuration. The cell was hermetically sealed using glass-to-metal seals, and incorporated a low pressure safety vent on the bottom of the cell case which would open at 150 psi. A description of the sealed cell is as follows:

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PRELIMINARY CELL DESIGN

CELL CASE: 1.135" diameter x 1.50" tall (1.5 in^3/27.25cc)
             304 Stainless steel
             Glass-to-metal seal
             150 psi safety vent

CATHODE: 90% Acetylene Black/10% Dupont Teflon
             12.5" x 0.95" x 0.022" (153 cm^3)
             Exmet expanded nickel grid

ANODE: Annealed calcium foil on expanded nickel
             grid 13.5" x 0.95" x 0.22"

SEPARATOR: Non-woven glass 0.012" thick
             Reeve Angel or Dexter

ELECTROLYTE: 1.0 molar LiAlCl$_4$/SOCl$_2$
             22 grams average

Efficiencies of the various electrodes, as well as changes in elect-

rolyte purification, molarity and preparation methods were evaluated in

these cells. Data from this first cell design was used to design a

second more optimized version of the cell. The second design differed

from the first in that the cathode thickness was reduced to increase

surface area of the electrodes by 30%. All cells used in the final

discharge characterization and safety investigation were constructed

using the optimum configuration with the same low pressure safety

vent assembly used in the first cell design.

OPTIMIZED CELL DESIGN

"HALF-D" CELL - 3.5 AH

CELL CASE: 1.135" diameter x 1.50" tall (1.5in^3/27.25cc)
               304 Stainless Steel
               Glass-to-metal seal
               150 psi Safety Vent

CATHODE: 90% Acetylene Black/10% Dupont Teflon
               15.5" x 1.0" x 0.017" (200 cm^2)

ANODE: Annealed calcium foil on expanded nickel
               grid. 16.0" x 1.0" x 0.012"

SEPARATOR: Non-woven glass 0.012" thick
               Reeve Angel or Dexter

ELECTROLYTE: 1.4 molar LiAlCl$_4$/SOCL$_2$
               22 grams average.

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All cells were activated using a vacuum system fabricated from teflon and glass, using approximately twenty-two (22) grams of 1.4 molar lithium aluminum tetrachloride/thionyl chloride.

A discussion of the development of the major cell structures is as follows:

a) Anode Development-Calcium anodes have been used extensively in thermal battery applications, both as sheet and vapor deposited; however, the use of these traditional electrodes was not practical with respect to the current design, the vapor deposited anode being too thin and the pure sheet being too brittle. Elemental calcium as manufactured is too brittle to be bent easily; and lamination to an expanded metal current collector is difficult. Preliminary discharge data using calcium anode was accumulated in laboratory bag cells using calcium film 0.015 inches thick as received from the manufacturer with a 0.125 inch wide nickel tab spot welded to the calcium foil as a current collector. Examination of these cells after discharge showed heavy corrosion at the sites of the spot welds resulting in extremely poor contact at the tab/calcium interface. An improvement in these results was made by annealing the calcium film in an inert atmosphere. The annealing was accomplished by heating the calcium foil to its first phase change temperature in an inert atmosphere followed by slow cooling. The resulting foil was malleable, easily bent, and lent itself to lamination with an expanded metal current collector. Once laminated, the calcium foil did become somewhat work-hardened again; however, the resulting anode structure was still more manageable than the untreated calcium foil. Discharge capacities and load voltages in cells constructed with annealed and unannealed calcium anodes were compared using laboratory bag cells identical in all respects except for the

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anode variation. All were subjected to a 27 ohm constant resistive load and were monitored to a cutoff voltage of 2.00 volts. Table 1 and Figure 1 clearly indicate an increased capacity from those cells containing annealed calcium.

TABLE 1

UNANNEALED VERSUS ANNEALED CALCIUM ANODES

	UNANNEALED ANODE				ANNEALED ANODE		
TEST CELL	ANODE THICKNESS	TIME ABOVE 2.0V	CAPACITY (MAH)	CELL NO.	ANODE THICKNESS	TIME ABOVE 2.0V	CAPACITY (MAH)
8	.010	1.50	75	13	.010	3.50	175
9	.015	1.75	87.5	14	.015	3.65	182.5
10	.020	1.70	85.0	15	.020	3.72	186

The increased capacity seemed primarily due to improved electrical contact at the calcium/current collector interface. Although the calcium foil was annealed in a vacuum oven, the annealing atmosphere was never pure enough to prevent some oxide or nitride formation. When removed from the vacuum oven, the calcium ranged from a medium to dark gray, always considerably darker than before processing. To examine the consequences of the filming, discharge tests were made using calcium in varying states of oxidation as given in Table 2. Anodes were used in three (3) forms: gray as removed from the oven; polished by sanding with fine emery cloth; and heavily filmed, by exposing the anode to a 75% RH atmosphere for 60 minutes. All were discharged through 27 ohms in bag cells (5 cm^2 electrodes). Table 2 indicates a general lack of sensitivity towards the condition of the anode surface, evidenced by the constant capacity produced by all samples.
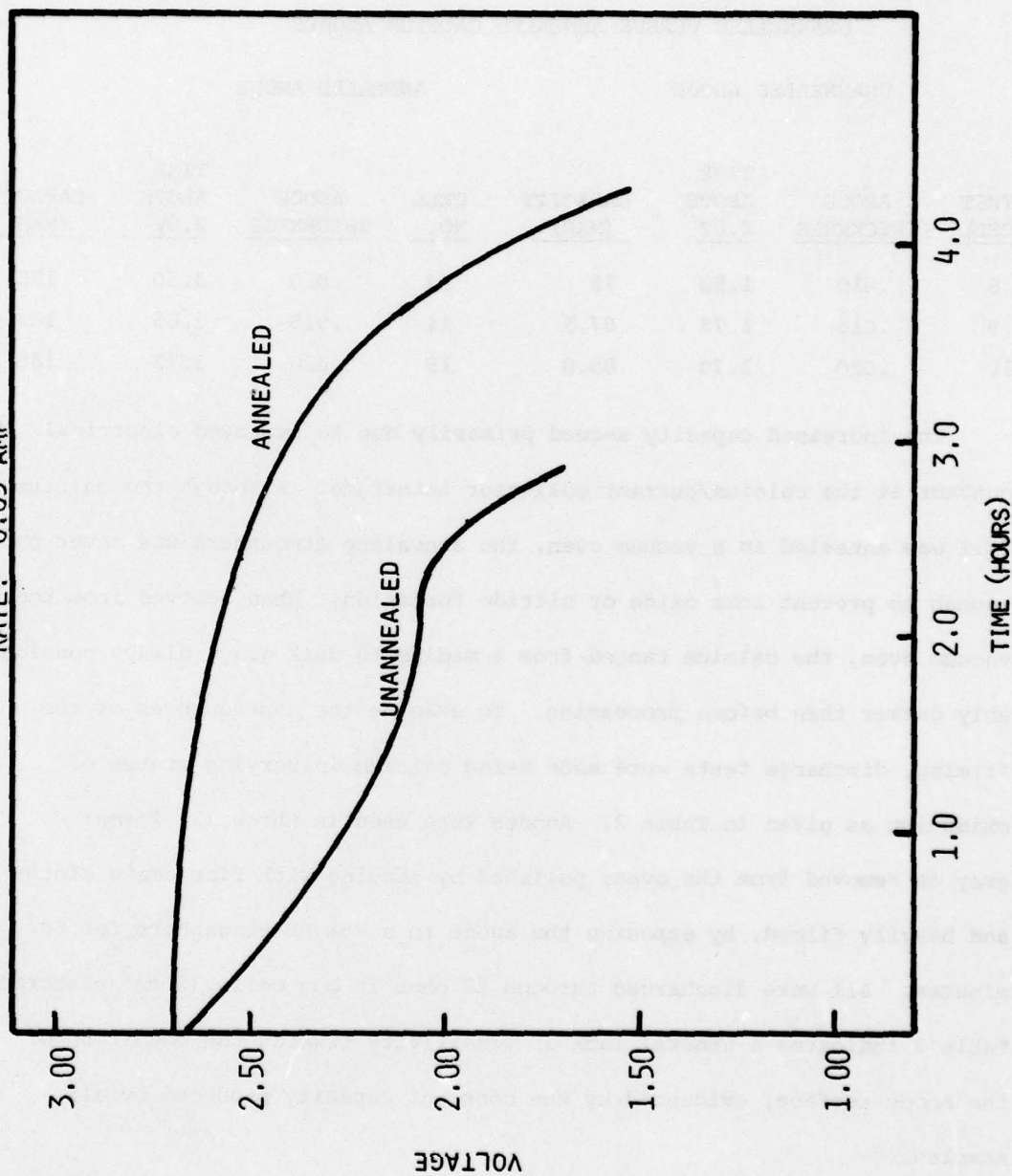
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FIGURE 1 CA/SOCL$_2$ OPEN LABORATORY CELLS ANNEALED VS. UNANNEALED CALCIUM-RATE: 0.05 AMP

TABLE 2

EFFECT OF ANODE SURFACE ON DISCHARGE

ANODE PREPARATION	SURFACE CONDITION	DISCHARGE TIME ABOVE 2.00 V
1) No preparation, used as received	Some film (med. gray)	45 minutes
2) Polished (with fine emery paper) surface slightly abraded.	Shiny, film removed	40 minutes
3) No preparation, exposed to 75% humidity for 60 minutes.	Heavily filmed, surface blackened	45 minutes

These results were observed repeatedly in an assortment of test vehicles throughout Phase I.

Based on these results, anodes used in sealed cells throughout the program have been used without any special care devoted to maintaining the original shiney surface.

b) Cathode Development - The original approach to the cathode for this system was to simply adapt the inert, teflon bound carbon black cathodes used in lithium/thionyl chloride cells to calcium/thionyl chloride. Initial discharges, however, indicated that a direct substitution of cathodes might not be practical, i.e. a cathode which works well with $Li/SOCl_2$ might not work well with $Ca/SOCl_2$. The first cells discharged yielded very poor cathode efficiency, a problem illustrated by the following matrix of nine (9) cells which utilized cathodes of varying thicknesses from 1.1 mm to 5.1 mm.

Cells were identical with the exception of cathode thickness, composed of 5 cm^2 electrodes and discharged in polyethylene bags. Throughout the range of current densities, the capacity of the cells remained constant
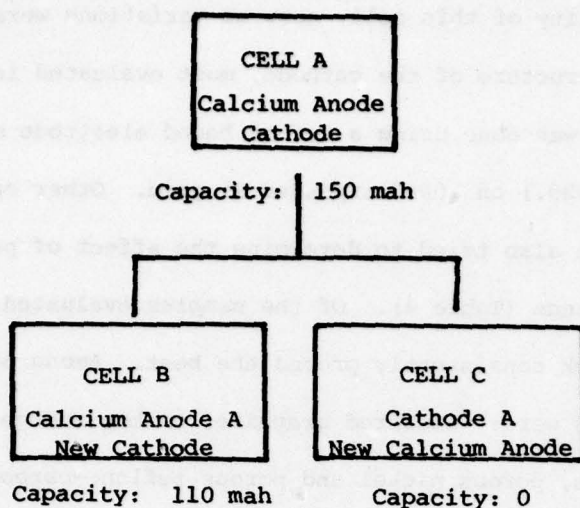
for all cathode thicknesses. Post mortem of the cells revealed them to be flooded with electrolyte and with excess calcium remaining at the anode, indicating that the source of the poor capacity might be the cathode.

TABLE 3

PRELIMINARY CURRENT DENSITY VS. CATHODE THICKNESS		
2.7 ma/cm^2	5.0 ma/cm^2	9.6 ma/cm^2
CATHODE THICKNESS		
1.3mm	Cap.* - 150 mah Voltage** - 2.87	Cap. - 155 mah Voltage - 2.60	Cap. - 70 mah Voltage - 2.54
2.5mm	Cap. - 145 mah Voltage - 2.80	Cap. - 172 mah Voltage - 2.70	Cap. - 70 mah Voltage - 2.55
5.1mm	Cap. - 156 mah Voltage - 2.84	Cap. - 170 mah Voltage - 2.70	Cap. - 72 mah Voltage - 2.60
Average Discharge Time	5.6 hours	3.4 hours	0.73 hours

* Above 2.0 volts
** Average Discharge Voltage

This assumption was verified in two ways. Three (3) electrode cells using a lithium wire as the third electrode revealed that cell failure was due to cathode polarization rather than anode. In addition, an electrode substitution test was made which indicated the cathode to be the failed electrode. The substitution test was made by discharging a bag cell until failure, then disassembling the cell and constructing two (2) new cells, one using the discharged anode with a fresh cathode, and a second using the discharged cathode with a new anode. Subsequent discharge of the two cells showed that no further capacity could be withdrawn from the discharged cathode, while the discharged anode produced almost as much capacity as during the original run.

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                    ┌─────────────────┐
                    │     CELL A       │
                    │  Calcium Anode   │
                    │     Cathode      │
                    └─────────────────┘

                    Capacity:  150 mah

        ┌─────────────────┐       ┌─────────────────┐
        │     CELL B       │       │     CELL C       │
        │ Calcium Anode A  │       │    Cathode A     │
        │   New Cathode    │       │ New Calcium Anode│
        └─────────────────┘       └─────────────────┘

        Capacity:  110 mah          Capacity:  0
```

The conclusions reached from these experiments were that the prime cause of reduced capacity from the system lay in premature cathode failure, and that the failure was probably caused by a clogging of the cathode with reaction products, presumably at the electrode surface. The penetration of the cathode seemed to be constant regardless of the thickness of the electrode.

Spent cathodes were examined and found to contain $CaCl_2$. A quantitative determination of the $CaCl_2$ present in a cathode which had produced 1.5 AH yielded 6.8 gms. This quantity is not unrealistic if the reaction mechanism considered is $SOCl_2 + Ca \longrightarrow CaCl_2 + So$, which would predict a $CaCl_2$ content of 7.25 grams after 3.5 AH. By comparison with the analogous lithium system, with which the problem cathodes performed well, an examination of reactant volumes predicted some loss in capacity.

Assuming the capacity limiting factor to be reactant volume and the overall energy producing reactions to be:

$$SOCl_2 + 2 Li \longrightarrow 2 LiCl + So$$
$$SOCl_2 + Ca \longrightarrow CaCl_2 + So$$
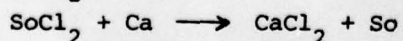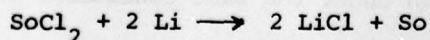
the volume of LiCl per AH is .77 cm^3 compared with 96 cm^3 $CaCl_2$ per AH. This alone predicts a 20% reduction in capacity.

Due to the low capacity of this cell, several variations were made in the composition and structure of the cathode, most evaluated in bag cells. The initial work was done using a teflon bound electrode of Columbian carbon black (929.) on .005" expanded Ni grid. Other carbon blacks and graphites were also tried to determine the effect of particle s i z e on cathode performance (Table 4). Of the samples evaluated, Shawinigan Acetylene Black consistently proved the best. Among other cathode samples evaluated were: sintered graphite, carbon sponge, carbon felt, carbon monofluoride, porous nickel and porous teflon--carbon--films. All suffered from low surface areas and all discharged at reduced voltage under load. Dry hot-formed electrodes, carbon black "pocket" plates formed by packing carbon mixtures into porous nickel envelopes, and pella-tized carbon formed by blending carbon black with alcohol were also tried but failed to produce a suitable cathode for the $Ca/SOCl_2$.

The cathodes used in half-D cells were made using teflon bound acetylene black. The cathodes were formed to a thickness of .022" to alleviate as much as possible the clogging effect noted in larger elect-rodes. The first sealed cells using this electrode had a surface area of 153 cm^2.

To cvaluate the cathode and anode, the "half-D" cells incorporated a lithium reference electrode. Normal discharge at room temperature indicated that the cathode was polarizing to a far greater extent than the anode. A plot of this data in Figure 2 shows cathode polarization going from 410 millivolts to 1010 millivolts with respect to the lithium reference elect-rode while anode polarization under the same conditions varied from 20 millivolts to 120 millivolts.

TABLE 4
CARBON BLACKS EVALUATED

CARBON TYPE	PARTICLE DIAMETER	STRUCTURE
Shawinigan Acetylene Black	42 nanometer	–
Degussa Corax	28	480
Huber N-339	23	128
Huber N-650	60	125
Huber N-765	23	103
Huber N-326	29	75
Huber N-762	76	65
Huber N-330	29	103
Ashland N-650	68	134
Ashland N-762	74	80
Ashland N-375	26	102
Ashland N-339	22	114
Cabot Monarch 1300	13	121
Cabot Monarch 1100	14	65
Cabot Monarch 880	16	120
Black Perl 1300	13	105
Black Perl 1100	14	50
Black Perl 880	16	110
Vulcan XC72	30	185
Vulcan XC72R	30	178
Regal 336	62	25
Regal 330R	62	70
Mineral Lamp Black 8405		
Mineral Carbon Black C391		
Mineral Water Dispersable Balck 8452		

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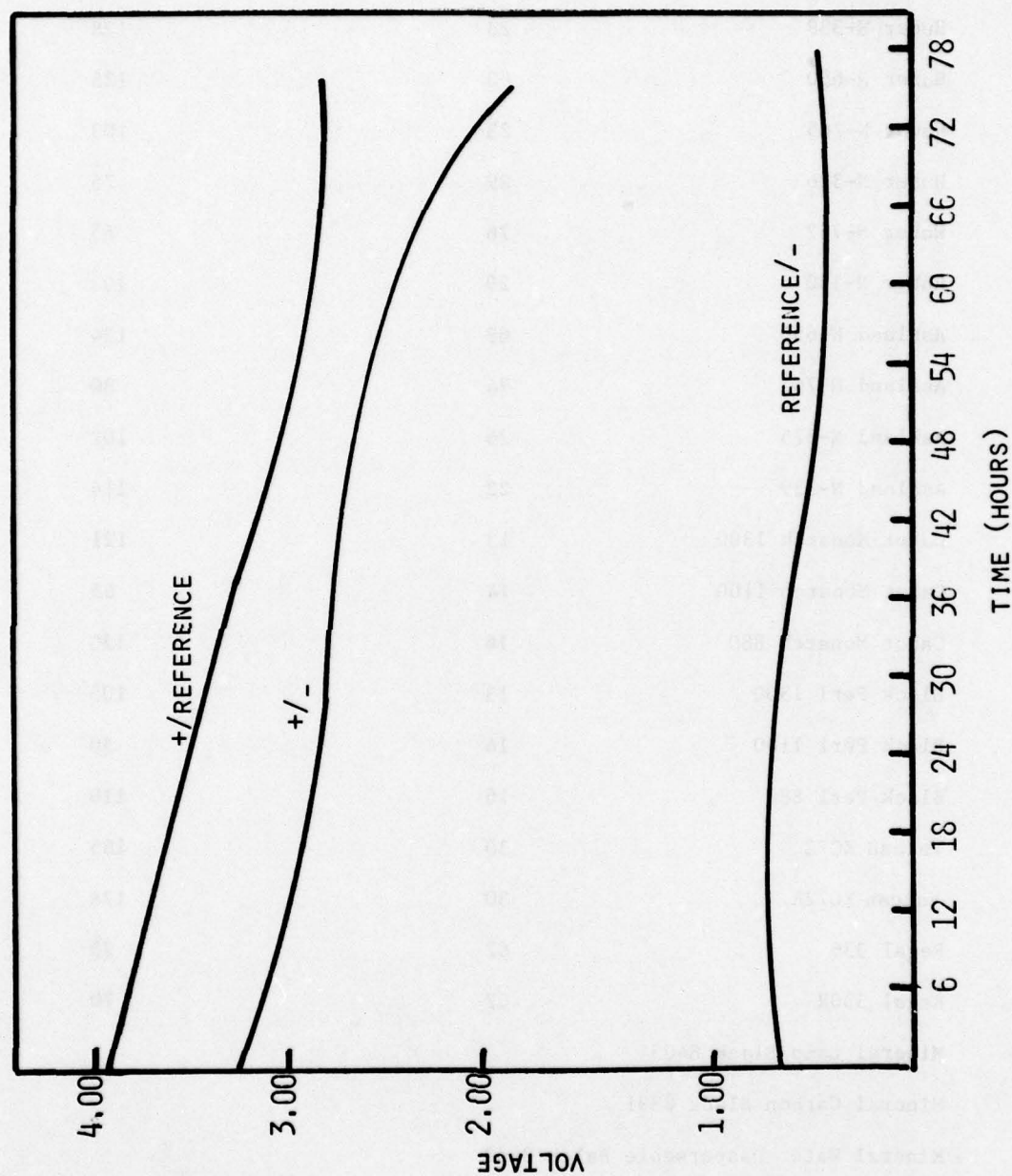CELL POLARIZATION
ROOM TEMPERATURE DISCHARGE
RATE: 0.05 AMP

FIGURE 2 CELL POLARIZATION - ROOM TEMPERATURE DISCHARGE - RATE: 0.05 AMP
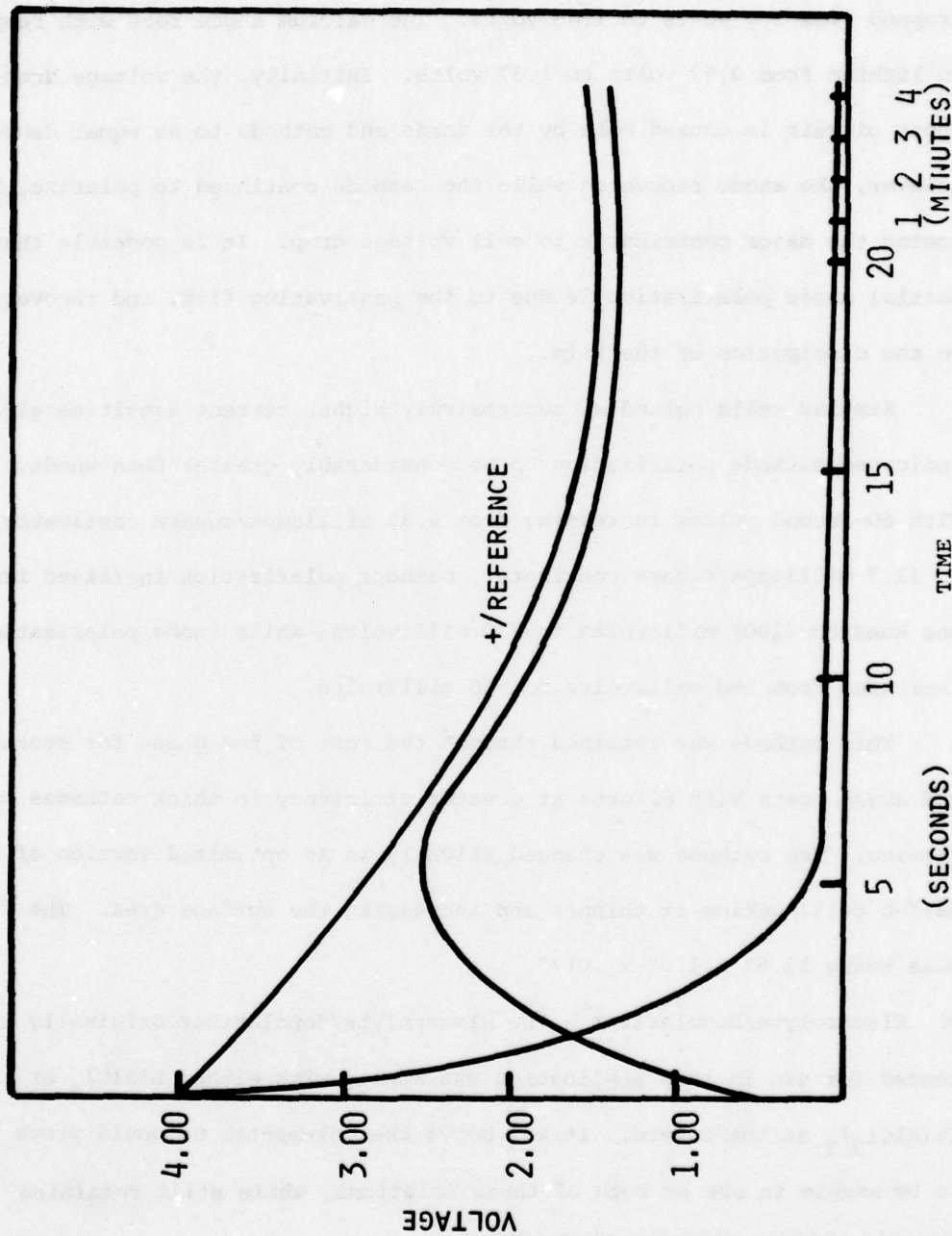
CELL POLARIZATION TEST
SHORT CIRCUIT TEST

FIGURE 3 CELL POLARIZATION TEST - SHORT CIRCUIT TEST

When these cells with reference electrodes were short circuited, the cathode also exhibited a greater degree of polarization. Figure 3 is representative of all cells tested. Half cell voltages stabilized within twenty (20) seconds. With respect to lithium, the cathode voltage dropped from 3.9 volts to 1.46 volts. The calcium anode rose with respect to lithium from 0.57 volts to 1.37 volts. Initially, the voltage drop on short circuit is caused both by the anode and cathode to an equal degree; however, the anode recovered while the cathode continued to polarize, becoming the major contributor to cell voltage drop. It is possible that initial anode polarization is due to the passivating film, and recovery to the dissipation of the film.

Similar cells pulsed at successively higher current densities also indicated cathode polarization to be considerably greater than anode. With 60-second pulses increasing from 0.35 milliamps/square centimeter to 11.7 milliamps/square centimeter, cathode polarization increased from one hundred (100) millivolts to 730 millivolts, while anode polarization increased from 180 millivolts to 500 millivolts.

This cathode was retained through the rest of the phase for storage and abuse tests with efforts at greater efficiency in thick cathodes continuing. The cathode was changed slightly in an optimized version of the half-D cell, making it thinner and increasing the surface area. The final size being 15.5" x 1.0" x .017".

c) Electrolyte/Depolarizer - The electrolyte/depolarizer originally intended for use in this application was $SOCl_2$, with either $LiAlCl_4$ or $Ca(AlCl_3)_2$ as the solute. It was hoped that elemental Ca would prove to be stable in one or both of these solutions, while still retaining a rapid voltage response when loaded.

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The electrolyte first used in bag cell discharges was $SOCl_2/LiAlCl_4$ and $SOCl_2/Ca(AlCl_3)_2$. Salts were iron free obtained from Fluke A.S., solvents were obtained from Eastman and re-distilled prior to use. These electrolyte solutions were used successfully in cells, discharging with the expected efficiency. However, in ampule tests of these solutions in contact with foil Ca samples (Table 5 & 6), the Ca filmed and in some cases generated enough gas to rupture the glass ampule after two (2) weeks storage at $50^{\circ}C$. Filming and/or decomposition of the Ca occurred only in salt solutions of $SOCl_2$ and not in the pure $SOCl_2$. Control ampules having Li samples instead of Ca generally showed less change in all solutions than those previously mentioned. None of the electrolyte samples were analyzed for water or other impurity contents. Molarities of the salt solutions were either .5M or 1.0M. One molar was used as the upper limit due to what seemed a limitation of $Ca(AlCl_3)_2$ solubility in the $SOCl_2$. Solutions of $Ca(AlCl_3)_2$ greater than 1.0 M produced a precipitate which went back into solution upon addition of $AlCl_3$.

A conductimetric titration was done by adding pure $CaCl_2$ to a 2.0 molal solution of $AlCl_3$ in $SOCl_3$ and monitoring the solution resistance using a 1 KHz AC resistance bridge. The resulting curve, Figure 4, indicates a stabilized conductivity and the onset of precipitation at an approximate mole ratio of 3 parts $AlCl_3$ to 1 part $CaCl_2$. The precipitate which occurred after the 3:1 ratio was reached was $CaCl_2$. This would seem to indicate that we were not seeing the expected $Ca(AlCl_3)_2$ species in $SOCl_2$ solution. A similar titration made by adding LiCl to a solution of $AlCl_3$ in $SOCl_2$ was performed with the expected results of a stable conductivity at a 1:1 mole ratio. The results of that titration was shown in Figure 5.

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MATERIAL COMPATIBILITY EVALUATION SUMMARY

ROOM TEMPERATURE

1 Month Test Period

TABLE 5

SAMPLE TESTED	SOCl$_2$	SO$_2$Cl$_2$	1.0m Ca(AlCl$_4$)$_2$/SOCl$_2$	1.0m Ca(AlCl$_4$)$_2$/SOCl$_2$	1.0m Ca(AlCl$_4$)$_2$/SOCl$_2$	1.0m LiAlCl$_4$/SOCl$_2$
1. Calcium strip-polished	Surface slightly darkened	Surface slightly darkened	Surface uniformly dark	Surface uniformly dark Edges corroded	Surface uniformly dark Edges corroded	Surface slightly darkened
2. Calcium strip-laminated to nickel grid-nickel tab spot-welded	Surface slightly darkened	Surface slightly darkened	Surface uniformly dark	Surface uniformly dark Edges corroded Spotweld attacked	Surface uniformly dark Edges corroded Spotweld attacked	Surface slightly darkened
3. Lithium strip	No change	No change	Edges slightly darkened	Edges darkened	No change	No change
4. Lithium strip-laminated to nickel grid-nickel tab spot-welded	No change	No change	Edges slightly darkened	Edges darkened	No change	No change
5. Nickel tab	No change	No change	No change	No change	No change	No change
6. Expanded nickel grid	No change	No change	No change	No change	No change	No change
7. 304 Stainless Steel	No change	No change	Mild discoloration	Mild discoloration	Mild discoloration	Mild discoloration
8. 304 Stainless Steel	No change	No change	Mild discoloration	Mild discoloration	Mild discoloration	Mild discoloration

TABLE 6

CALCIUM STABILITY STUDY – 120°F

SOLVENT	POLISHED			UNPREPARED		
	24 Hours	7 Days	14 Days	24 Hours	7 Days	14 Days
1.0 $SOCl_2$ Pure	Slightly gray Some dulling of finish	No change	No change	No change	No change	No change
2.0 $SOCl_2$ 0.5m $Ca(AlCl_4)_2$	Slightly gray Some dulling of finish	Blackened uniformly 50% corrosion	Surface uniformly black 75% corrosion flaky residue in solvent	No apparent change	Surface uniformly blackened 50% corrosion	Surface uniformly blackened 75% corroded flaky residue in solvent
3.0 $SOCl_2$ 1.0m $Ca(AlCl_4)_2$	Slightly grey Some dulling of finish	Surface uniformly blackened 75% corrosion flaky residue in solvent	Sample completely decomposed heavy residue	No apparent change	Surface uniformly blackened 75% corroded	Sample completely decomposed heavy residue
4.0 $SOCl_2$ 1.0m $Ca(AlCl_4)_2$	Slightly duller finish	Surface uniformly black Some corrosion along edges No residue	Unchanged No residue	No obvious change	Surface uniformly black Some corrosion on edges, No residue	Unchanged
5.0 SO_2Cl_2 0.5m $Ca(AlCl_4)_2$	Sample blackened heavy corrosion	Sample exploded 36 – 48 hrs. into storage	Sample exploded 36 – 48 hrs. into storage	Sample blackened heavy corrosion	Sample exploded 36 – 48 hrs. into storage	Sample exploded 36 – 48 hrs. into storage

CONDUCTIMETRIC TITRATION
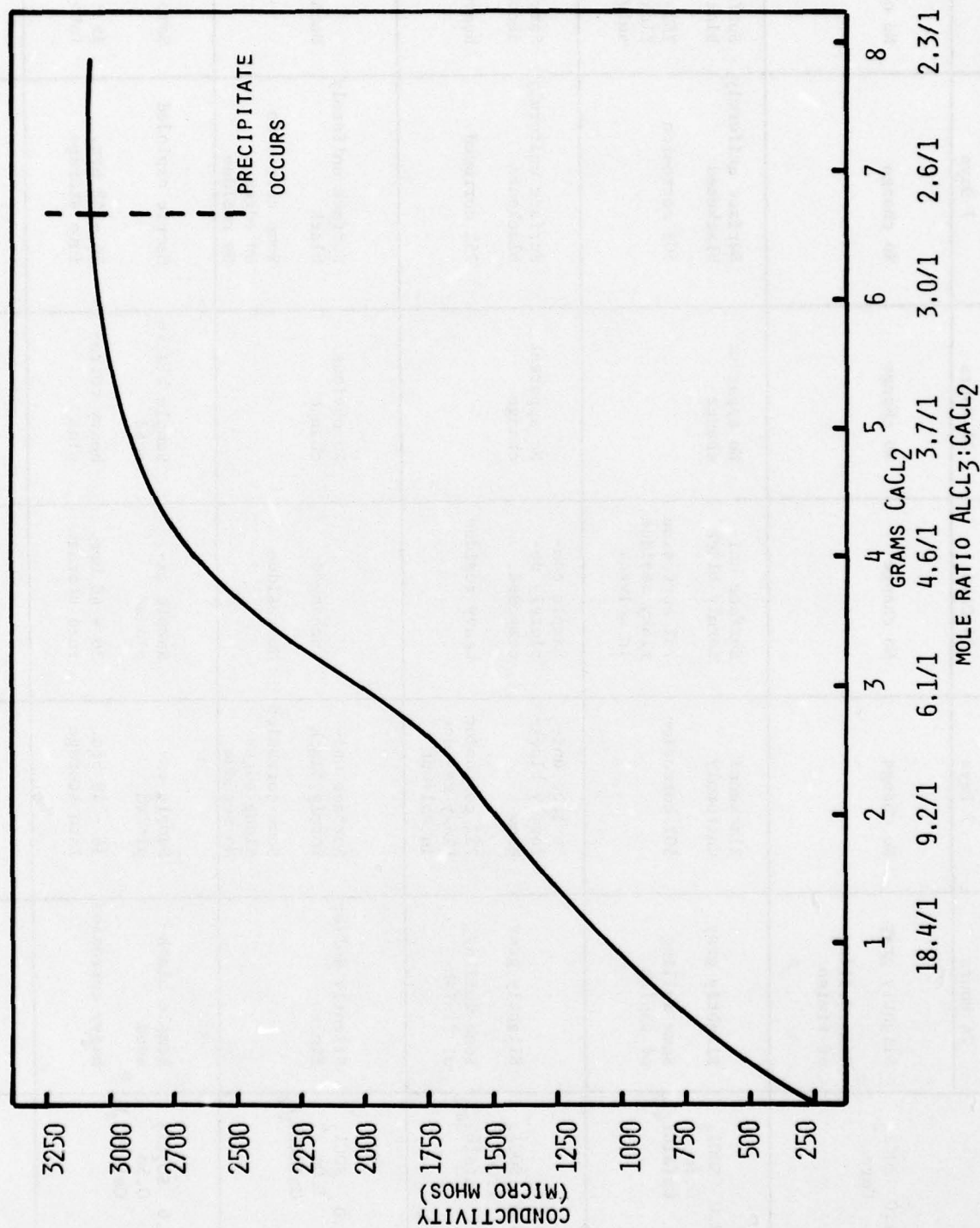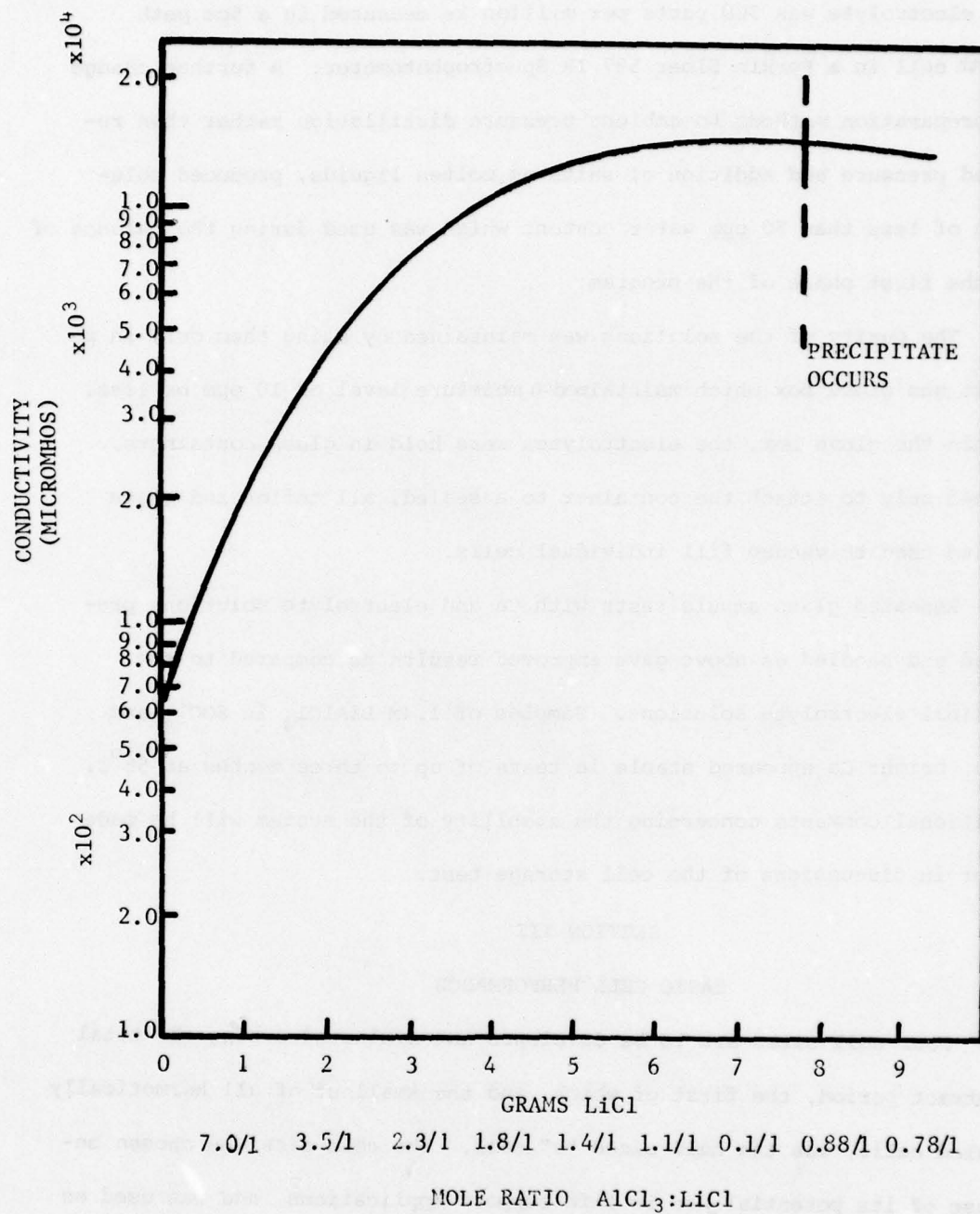

FIGURE 4 CONDUCTIMETRIC TITRATION

-20-

Figure 5 CONDUCTIMETRIC TITRATION

$AlCl_3/LiCl$

A modified distillation procedure was used to prepare $SOCl_2$ for use in sealed "half-D" cells, 1.4 molar in $LiAlCl_4$. Water content of the electrolyte was 300 parts per million as measured in a 5cm path length cell in a Perkin Elmer 597 IR Spectrophotometer. A further change in preparation methods to ambient pressure distillation rather than reduced pressure and addition of salts as molten liquids, produced solution of less than 50 ppm water content which was used during the balance of of the first phase of the program.

The purity of the solutions was maintained by using them only in an inert gas glove box which maintained a moisture level of 10 ppm or less. Within the glove box, the electrolytes were held in glass containers, opened only to attach the container to a sealed, all teflon and glass system used to vacuum fill individual cells.

Repeated glass ampule tests with Ca and electrolyte solutions prepared and handled as above gave improved results as compared to the original electrolyte solutions. Samples of 1.4M $LiAlCl_4$ in $SOCl_4$ and pure, bright Ca appeared stable in tests of up to three months at $55^{\circ}C$. Additional comments concerning the stability of the system will be made later in discussions of the cell storage test.

SECTION III

BASIC CELL PERFORMANCE

Four cell sizes are to be developed and evaluated during the total contract period, the first of which, and the smallest of all hermetically sealed cells, was the half sized "D" cell. The cell size was chosen because of its potential use in life support applications, and was used as a primary vehicle for evaluating the $Ca/SOCl_2$ system because of its small

size and therefore greater safety as well as its simplicity and ease of construction.

This cell was used in three ways during the course of this first phase: as a tool for general evaluation of the system; as a standard cell to evaluate storage capabilities; and as a standard cell for use in abuse tests.

The first design for the "half-D" cell was a cylindrical roll cell, as shown in Figure 6, contained in a 304 stainless case. The cell case had a glass-to-metal seal terminal pin and fill tube in the cover, and a 125 psi pressure release vent in the bottom. The cathode dimensions of this first design were 12.5" x 0.95" x .017". Composition was 90% acetylene black and 10% teflon on nickel Exmet. The separator was Dexter non-woven glass and the electrolyte was 22 grams of 1.0M $LiAlCl_4$ in $SOCl_2$. The anode was .020" Ca foil.

The cells were discharged according to the test schedule shown in Table 7; however the results of the discharges were erratic with capacities ranging from 3.0 AH to 1.0. A group of Li anode cells built under the same conditions and with the same electrolyte produced similarly erratic results. Upon examination of the electrolyte solution, the water content proved to be 300 ppm.

A second group of cells were prepared using a new electrolyte solution and different electrode balance for re-test. This group of cells had the same overall dimensions as the first, but had cathode dimensions of 15.5" x 1.0" x .017", Ca thickness of .013", and 22 grams of 1.4M $LiAlCl_4$ in $SOCl_2$, distilled by a different method and having a water, or hydrolysis product, content of less than 50 ppm.

-23-

TABLE 7
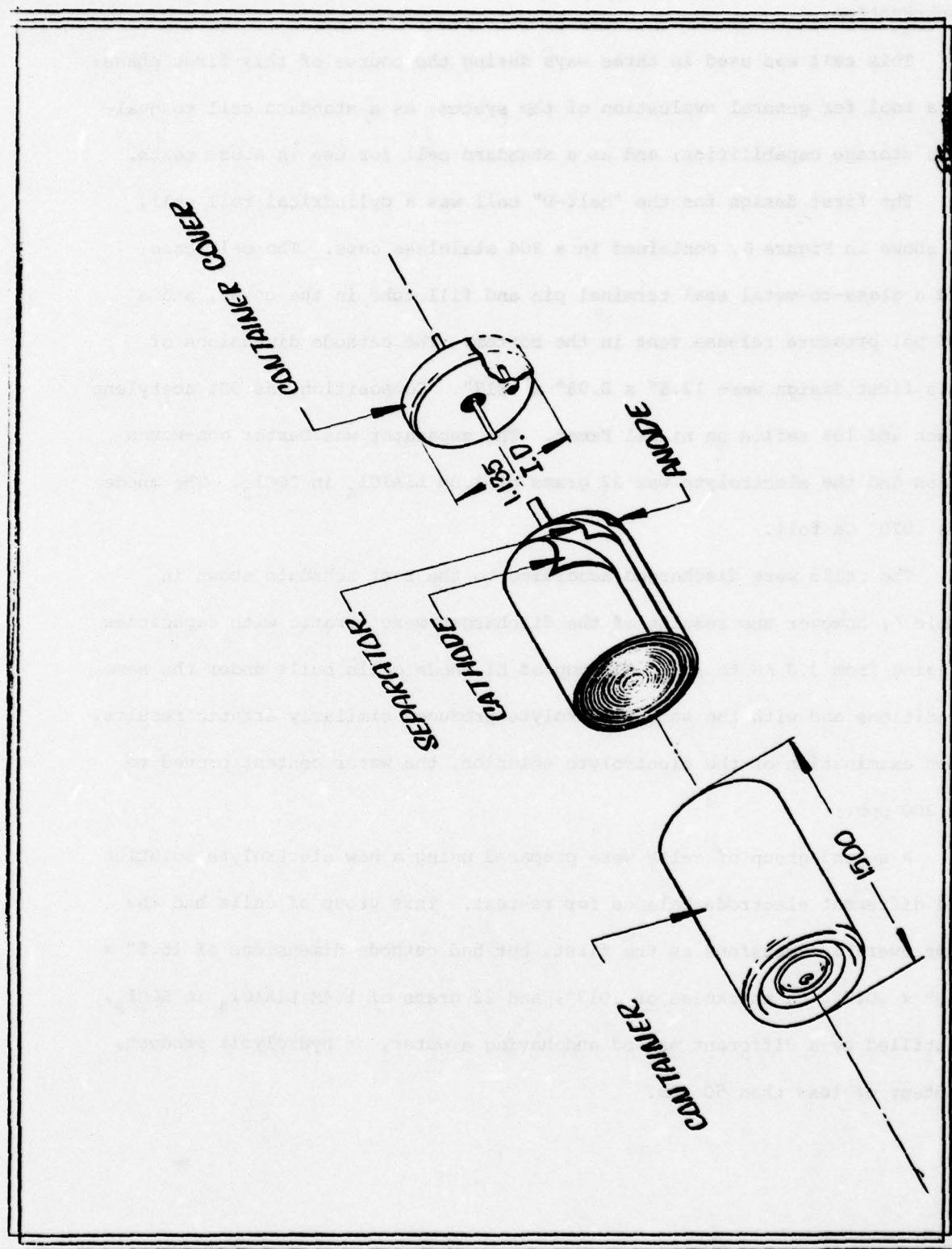
DISCHARGE MATRIX

Current Density		.25 ma/cm^2	.50 ma/cm^2	2.5 ma/cm^2	5.0 ma/cm^2
	-20°	2	2	2	2
	0°	2	2	2	2
Temperature	75°	4	4	4	4
	120°	2	2	2	2
	165°	2	2	2	2

This second group of cells was also discharged according to the matrix shown in Table 7, the referenced current densities of that table corresponding to a total cell current of 50 ma, 100 ma, 500 ma and 1000 ma respectively. Discharge of cells at 75°F at the four referenced rates is shown in Figure 7 - 10. A summary of the effects of current on capacity is given in Figure 11. A comparison of the second cell group against the first at a 40 ma discharge rate at 75°F is shown in Figure 12.

The nominal capacity of the cells at room temperature when discharged at a current of 50 ma (equivalent to .25 ma/in^2) was 3.5 AH. Open circuit was 3.1 volts and internal resistance measured in a 1 K Hz milliohmmeter. ranged from 600 to 800 mohms. The 3.5 AH capacity at 50 ma was reduced to approximately 2.25 AH when discharged at 1000 ma. The cells were discharged in open air and allowed to cool without restriction during discharge. No significant temperature rise was observed at 50, and 100ma rates, however a slight rise was noted at 500 ma rate, and there was a noticeable rise at the 1000 ma rate. At room temperature starting conditions, temperatures on the side of the cell case rose 28°F during the first 10-15 minutes of the 1000 ma discharge and stabilized at that temperature during the balance of the discharge. This rise in temperature is probably responsible for the relative consistancy of the load voltages at various rates.

A summary of cell discharges at 50 ma to 1000 ma rates at temperature other than 75°F is given in Figure 13. Discharges at -20°F are not shown as the cells would not run above 2.0 volts. Teardown and examination of the cells revealed that water content of the electrolyte solution was much higher than that normally found. Another group of cells was tried later in the program at -20°F and were found to discharge above 2.0 volts at the

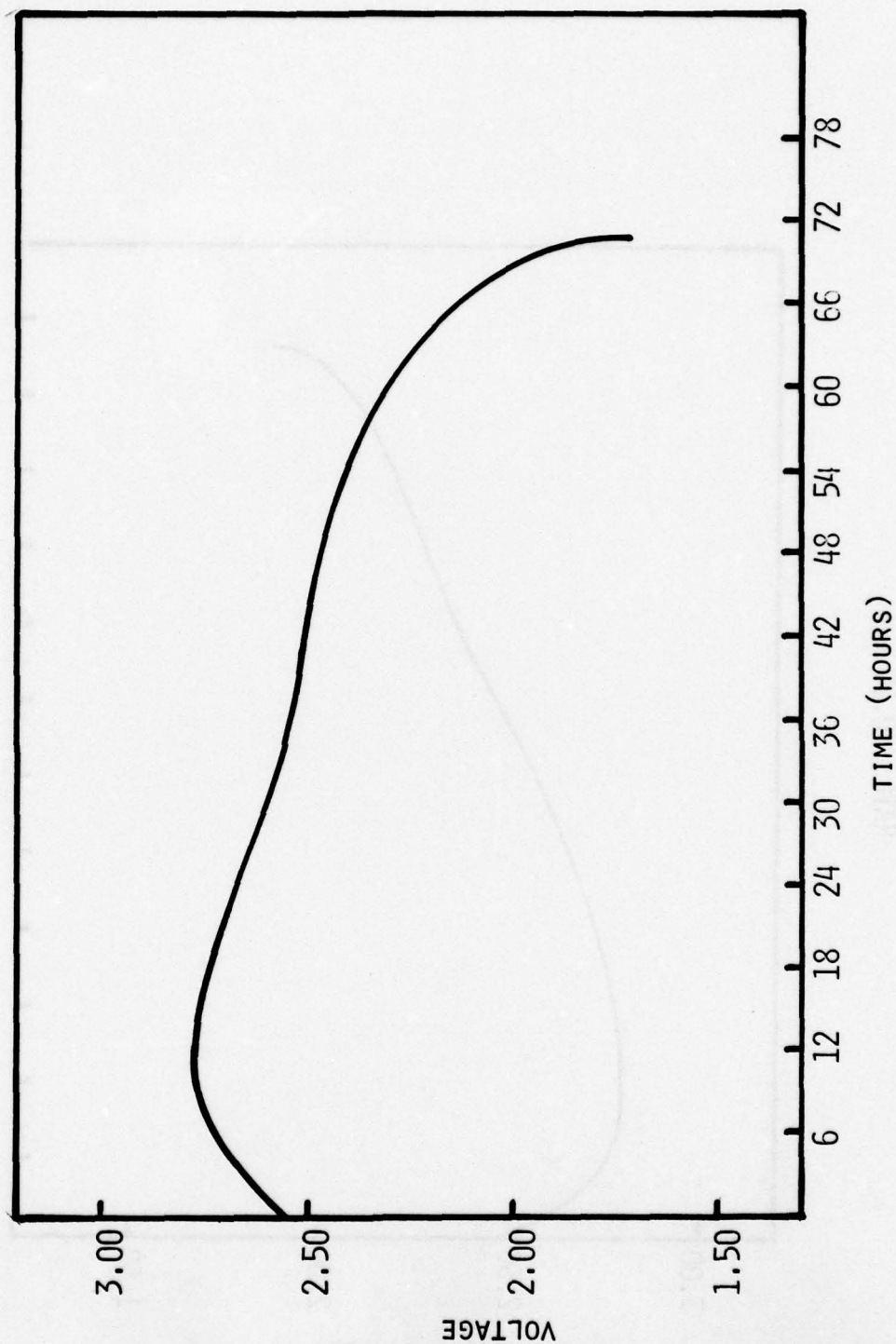-26-

Ca/SOCL$_2$
DISCHARGE CURVE
ROOM TEMPERATURE
RATE: 0.05 AMP

TIME (HOURS)

VOLTAGE

FIGURE 7 Ca/SOCL$_2$ DISCHARGE CURVE ROOM TEMPERATURE – RATE:0.05 AMP

CA/SOCL$_2$

DISCHARGE CURVE
ROOM TEMPERATURE
RATE: 0.10 AMP

VOLTAGE

3.00

2.50

2.00
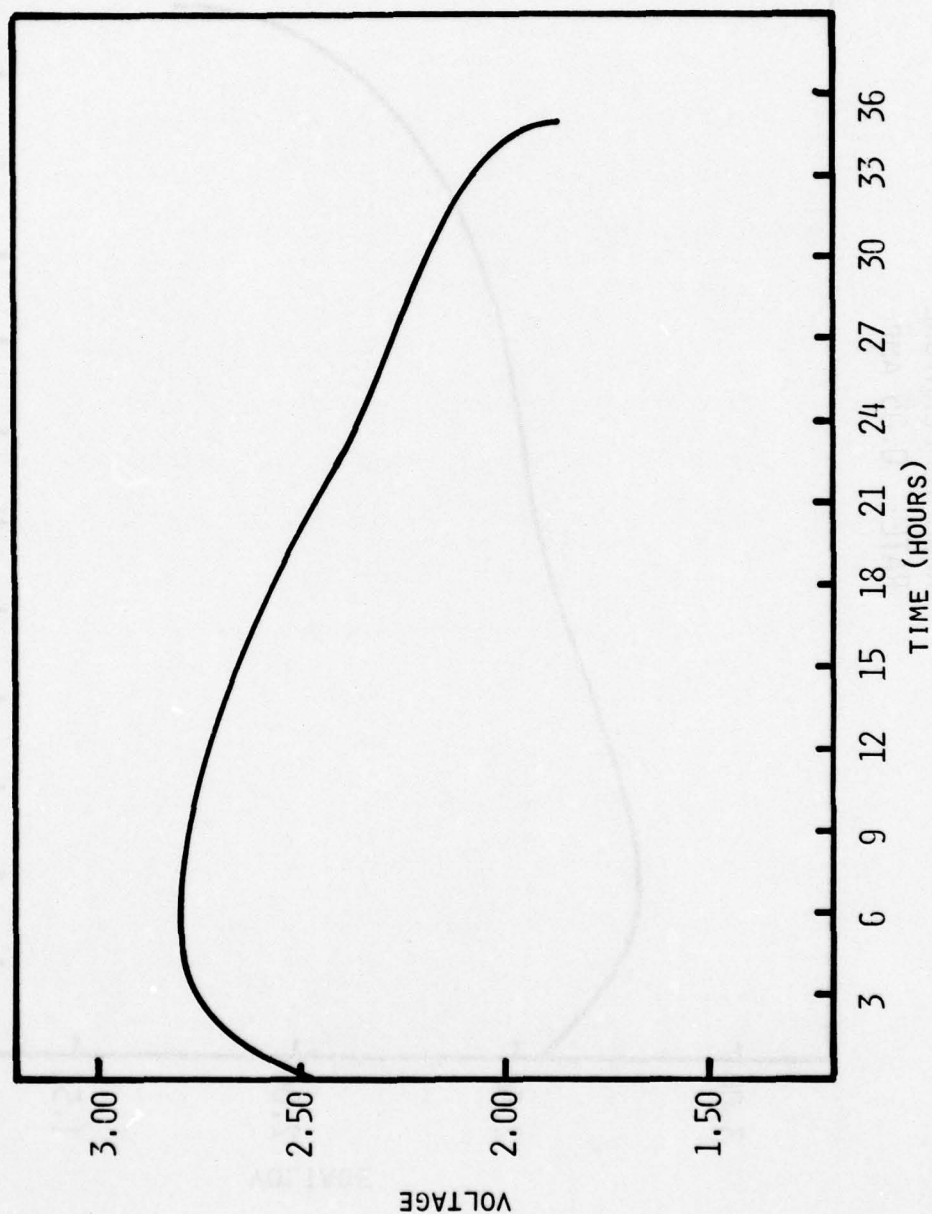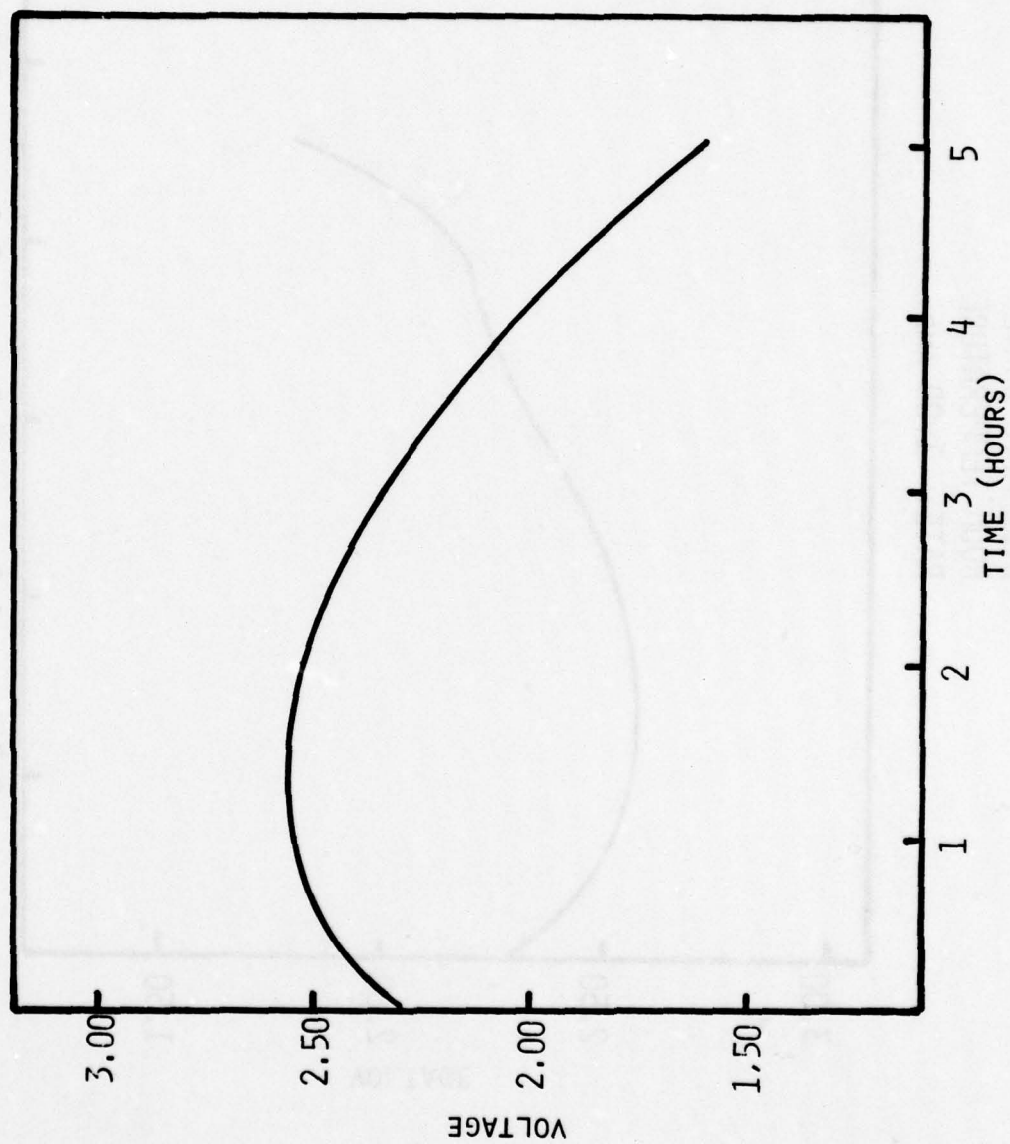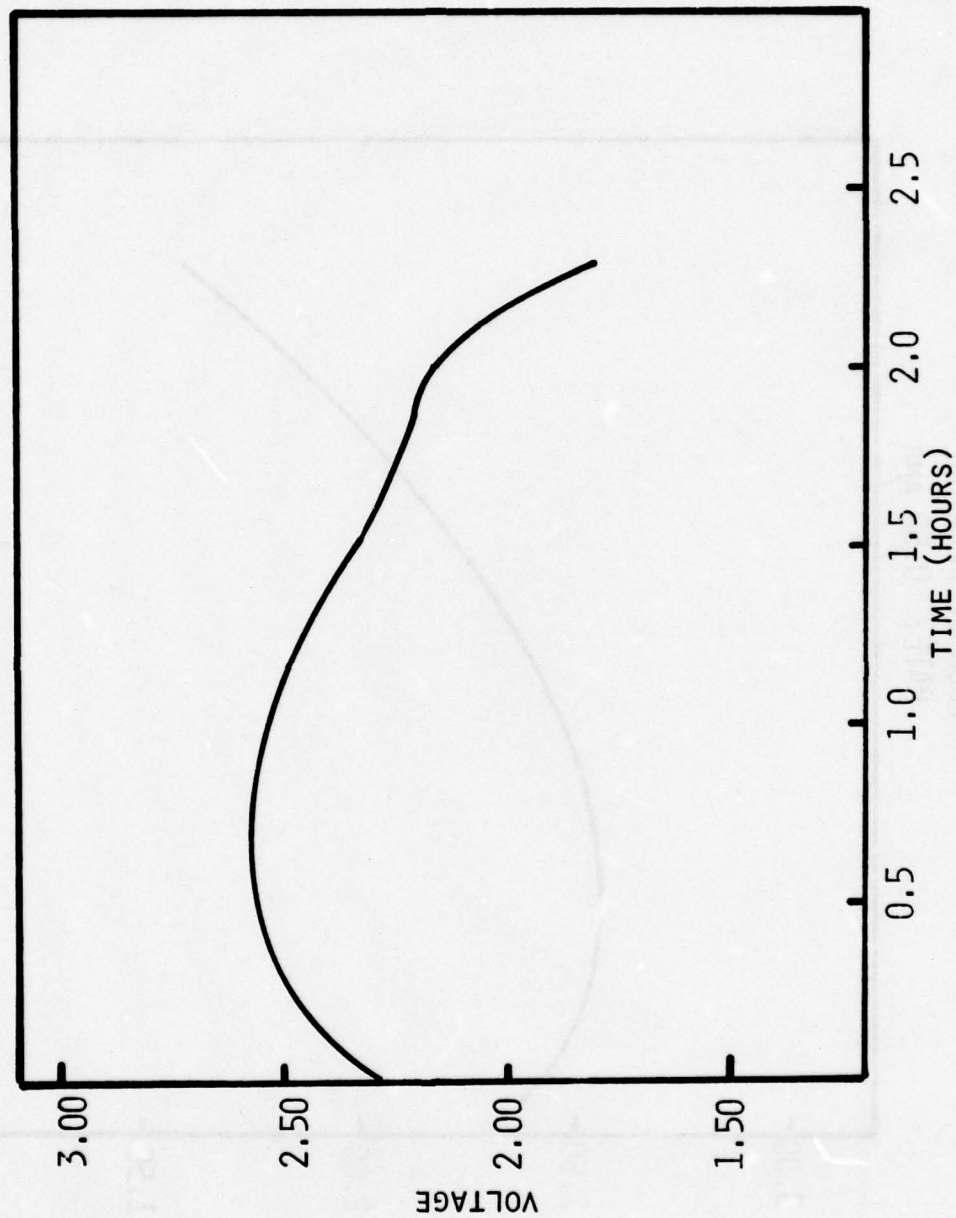
1.50

3 6 9 12 15 18 21 24 27 30 33 36

TIME (HOURS)

FIGURE 3 CA/SOCL$_2$ DISCHARGE CURVE ROOM TEMPERATURE - RATE: 0.10 AMP

Ca/SOCL$_2$

DISCHARGE CURVE
ROOM TEMPERATURE
RATE: 0.50 AMP

FIGURE 9 Ca/SOCL$_2$ DISCHARGE CURVE ROOM TEMPERATURE - RATE: 0.50 AMP

Ca/SOCl$_2$

DISCHARGE CURVE
ROOM TEMPERATURE
RATE: 1.00 AMP

FIGURE 10 Ca/SOCl$_2$ DISCHARGE CURVE ROOM TEMPERATURE – RATE: 1.00 AMP

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CA/SOCL$_2$
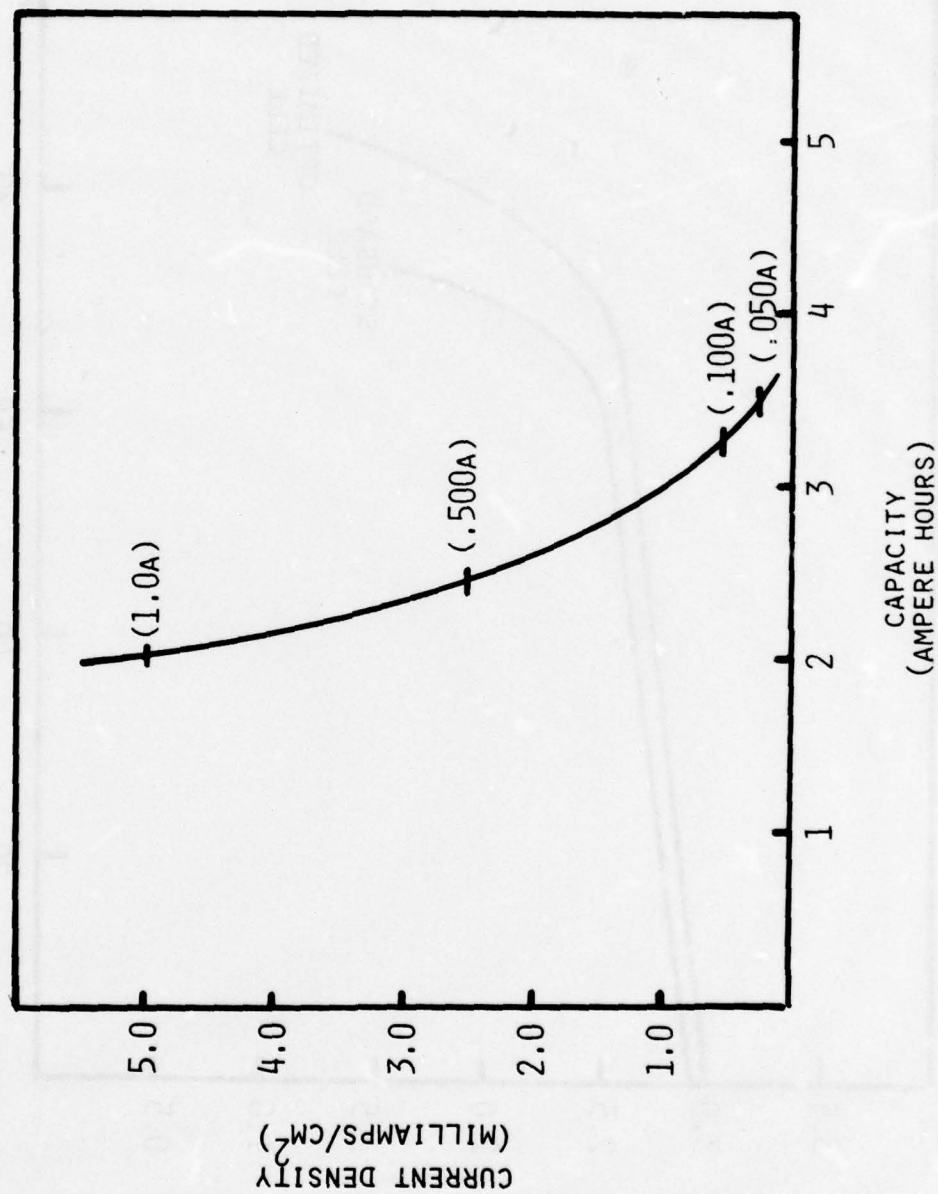
CAPACITY VERSUS CURRENT DENSITY
OPTIMIZED "HALF-D" CELL

FIGURE 11 CA/SOCL$_2$ CAPACITY VERSUS CURRENT DENSITY OPTIMIZED "HALF-D" CELL

-31-

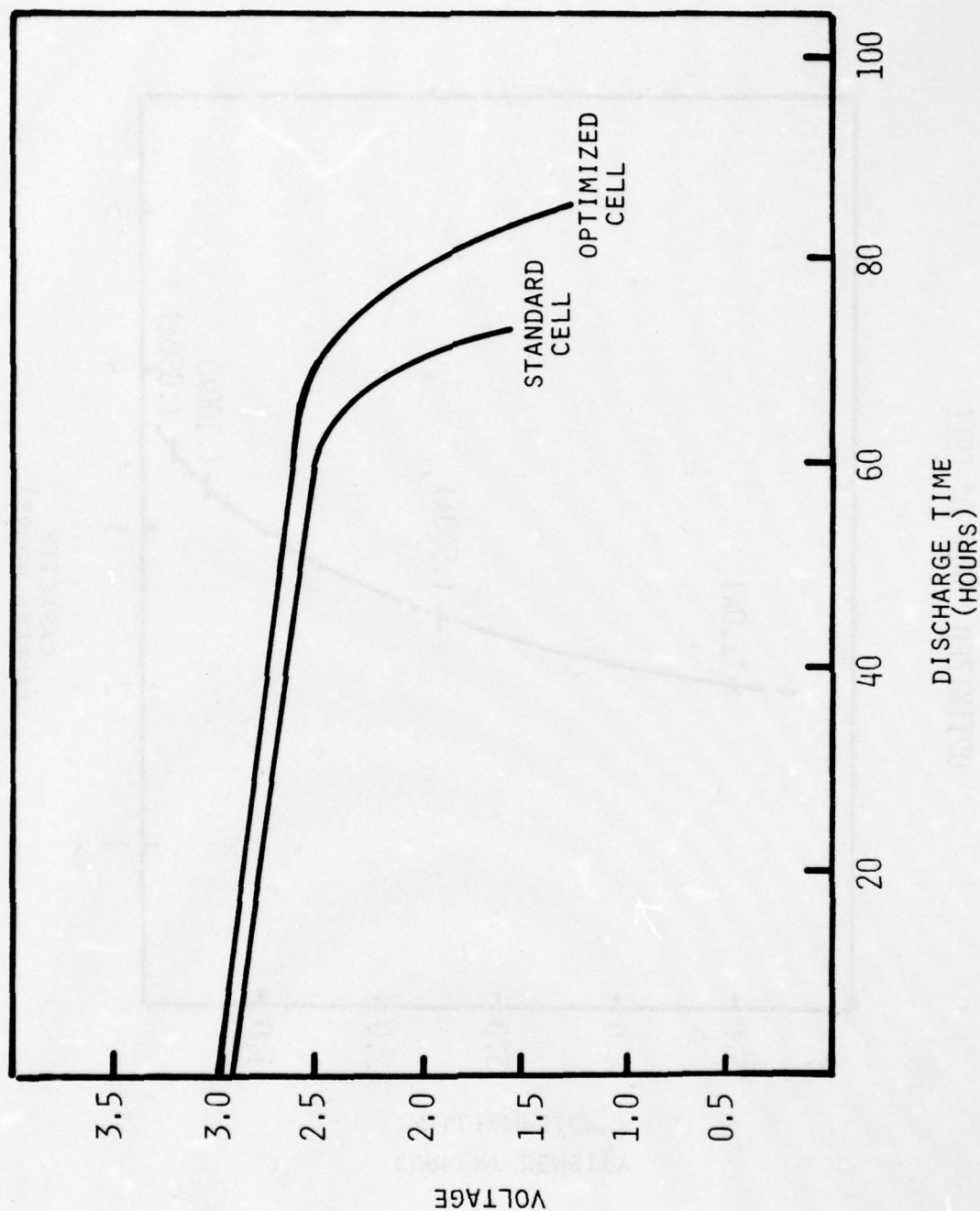Ca/SOCL$_2$

NORMAL DISCHARGE FOR "HALF-D" CELLS

FIGURE 12 Ca/SOCL$_2$ NORMAL DISCHARGE FOR "HALF-D" CELLS

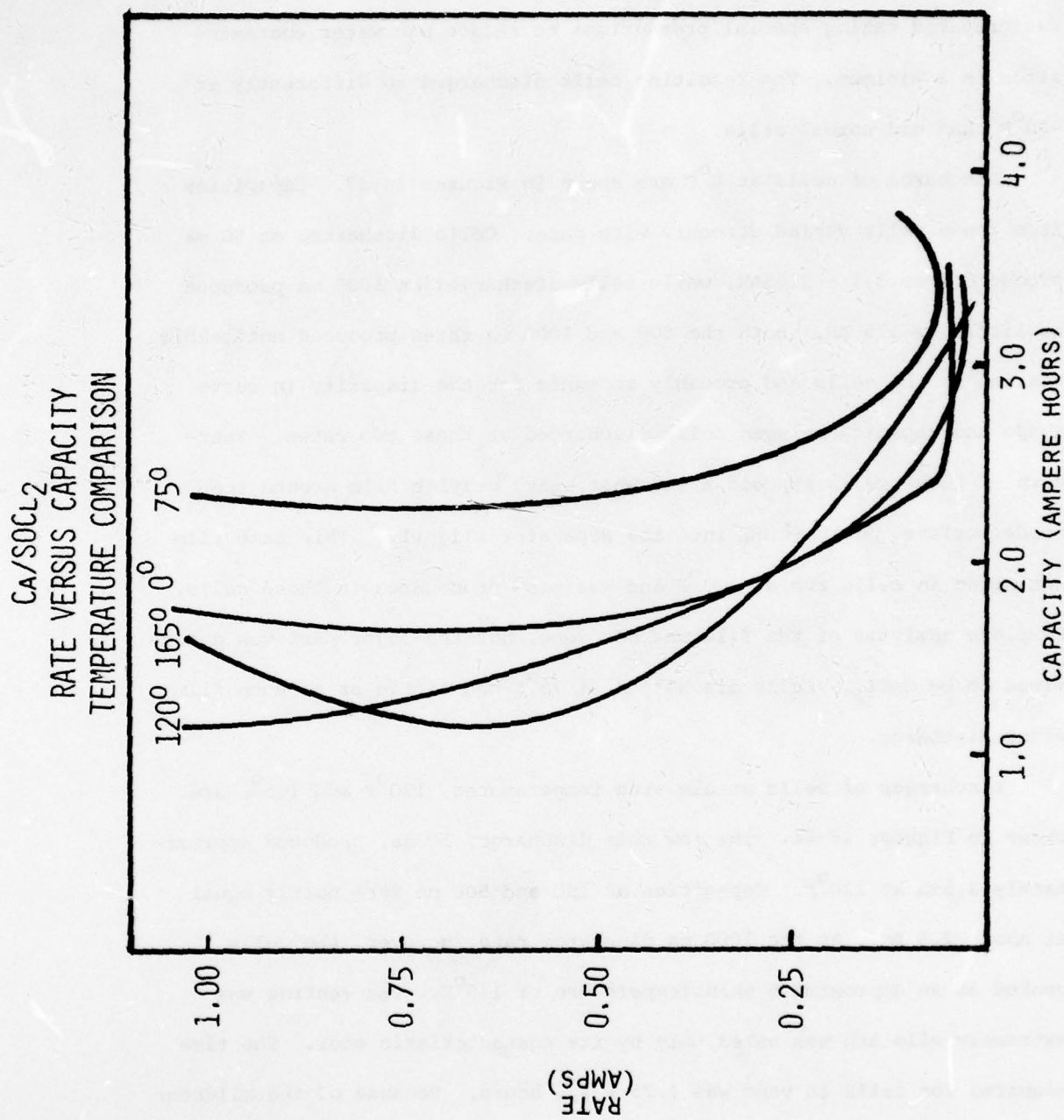# Ca/SOCL₂
RATE VERSUS CAPACITY
TEMPERATURE COMPARISON

FIGURE 13 Ca/SOCL₂ RATE VERSUS CAPACITY TEMPERATURE COMPARISON

-33-

50 ma rate but not at the higher rates. Discharge at -20°F produced 2.5 AH above 2.0 volts. Since moisture content seemed to affect the low temperature preformance of the cell, an additional group of cells was prepared taking special precautions to reduce any water contamination to a minimum. The resulting cells discharged no differently at -20°F than did normal cells.

Discharge of cells at 0°F are shown in Figures 14-17. Capacities from these cells varied strongly with rate. Cells discharged at 50 ma produced from 3.1 - 3.55AH, while cells discharged at 1000 ma produced as little as 1.5 AH. Both the 500 and 1000 ma rates produced noticeable heating in the cells and probably accounts for the disparity in curve shape and capacity between cells discharged at these two rates. Teardown of these cells exposed a somewhat heavy grayish film around the anode surface, penetrating into the separator slightly. This same film was noted in cells run at -20°F and was more promounced in those cells. Complete analysis of the film was not done, but the major part was determined to be $CaCl_2$. Cells discharged at 75°F had little or no such film after discharge.

Discharges of cells at elevated temperatures, 120°F and 165°F are shown in Figures 18-21. The low rate discharge, 50 ma, produced approximately 3.5AH at 120°F. Capacities at 100 and 500 ma were nearly equal at about 2.5 AH. At the 1000 ma discharge rate, however, the cells vented at an approximate skin temperature of 175°F. The venting was extremely mild and was noted only by its characteristic odor. The time required for cells to vent was 1.25 - 1.3 hours. Because of the mildness of the vent, it was thought that the cells might have been overfilled with

CA/SOCL$_2$
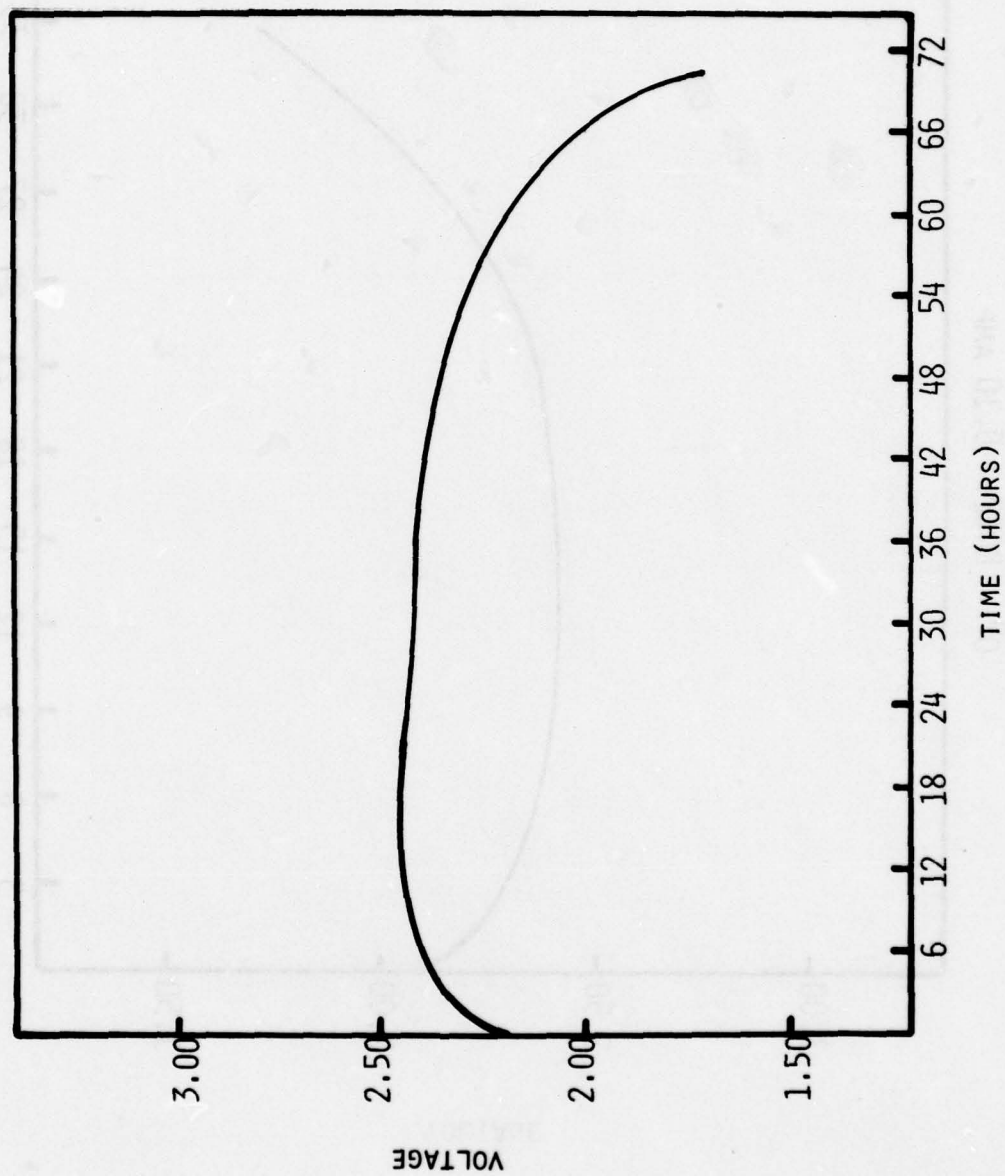DISCHARGE CURVE
0°F RATE: 0.05 AMP

FIGURE 14 CA/SOCL$_2$ DISCHARGE CURVE 0°F - RATE: 0.05 AMP
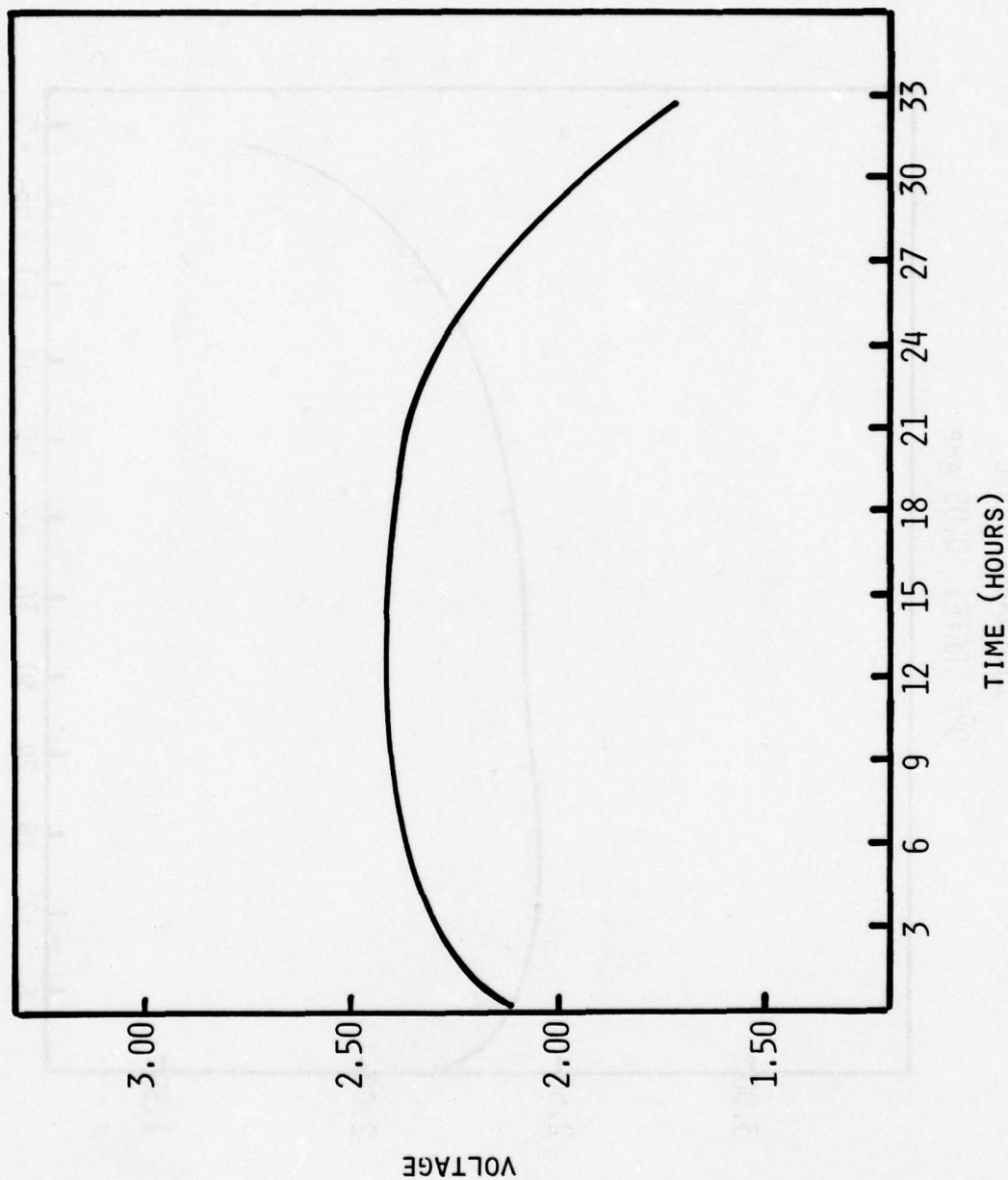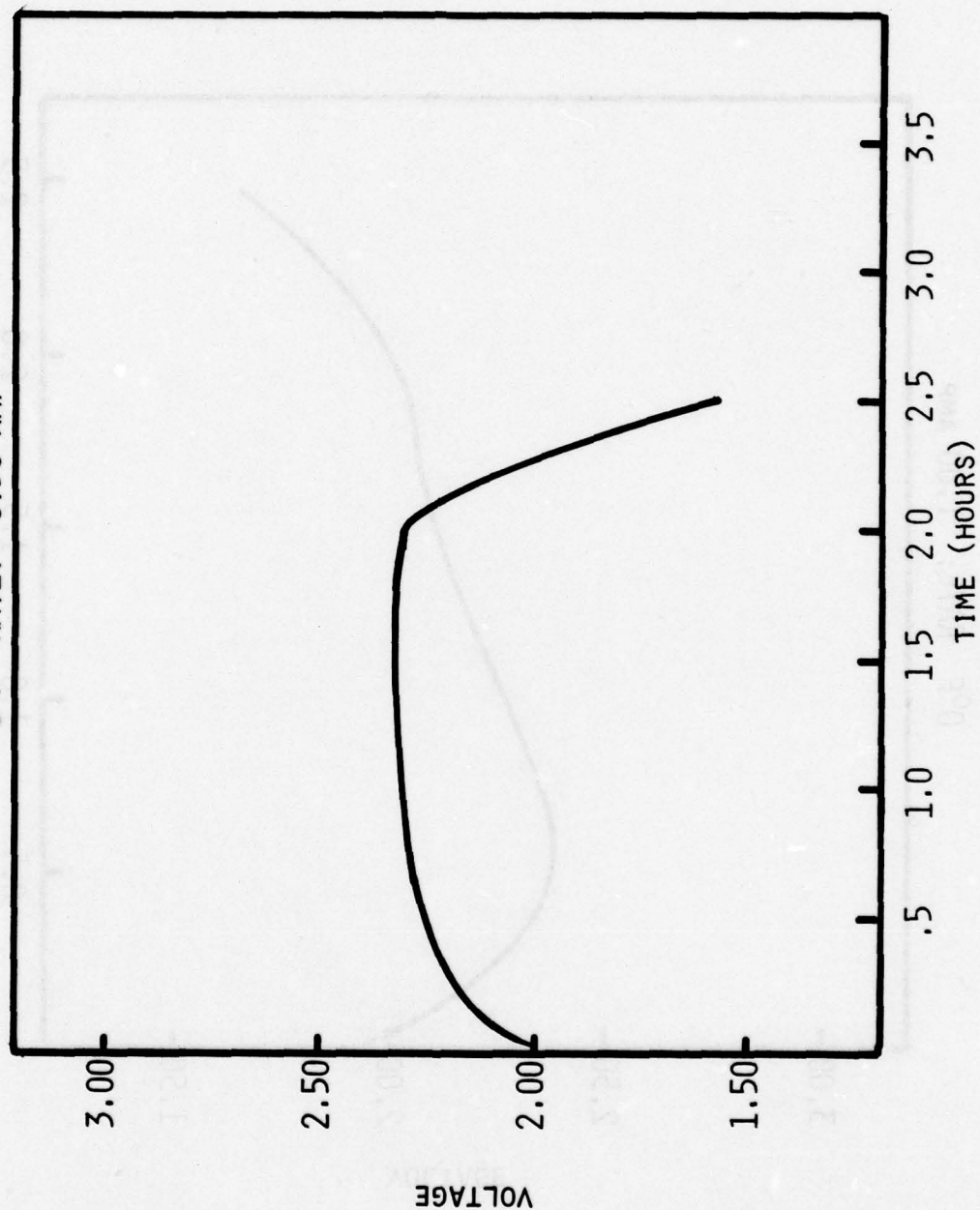
Ca/SOCL$_2$

DISCHARGE CURVE

0°F RATE: 0.10 AMP

FIGURE 15 Ca/SOCL$_2$ DISCHARGE CURVE 0°F - RATE: 0.10 AMP

TIME (HOURS)

VOLTAGE

-36-

FIGURE 16 Ca/SOCL$_2$ DISCHARGE CURVE 0°F-RATE: 0.50 AMP

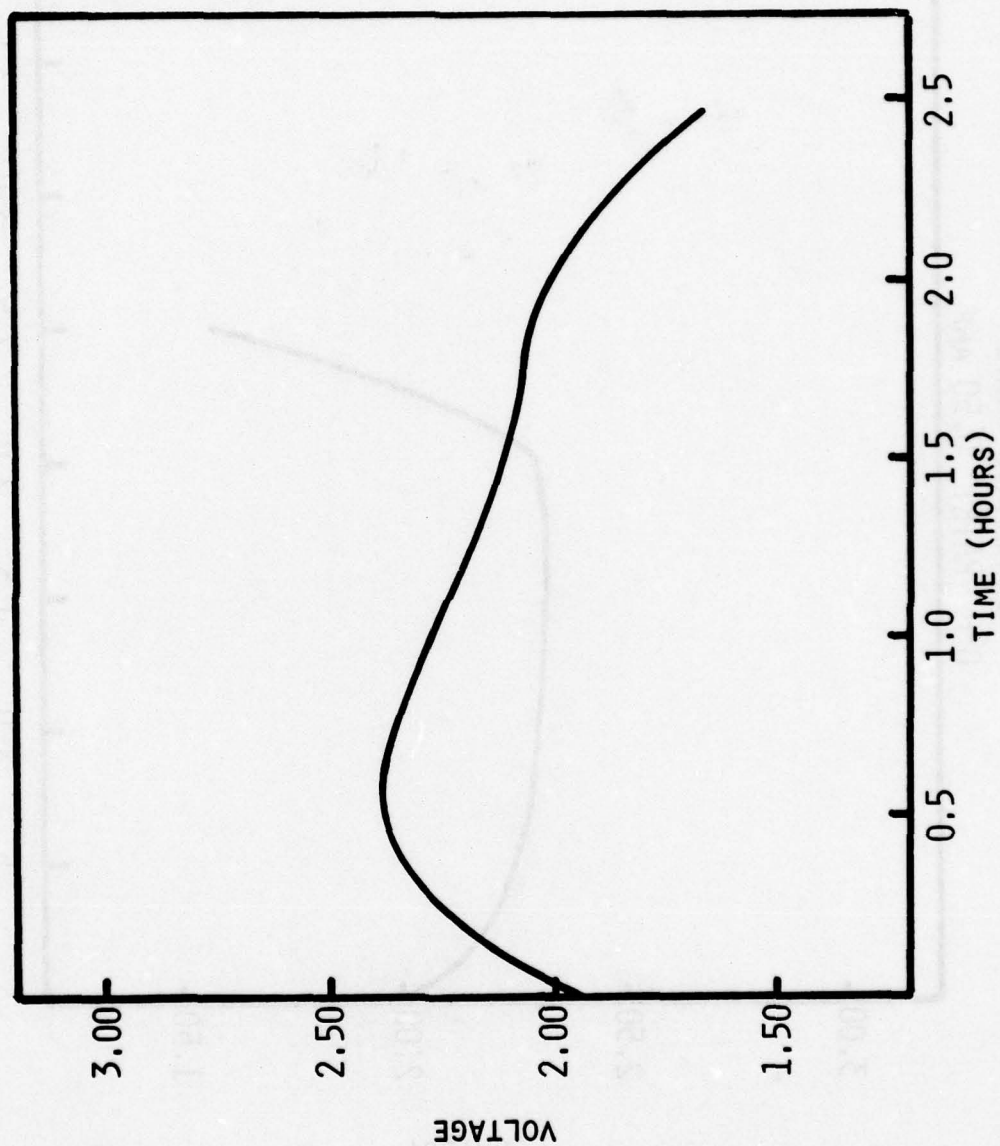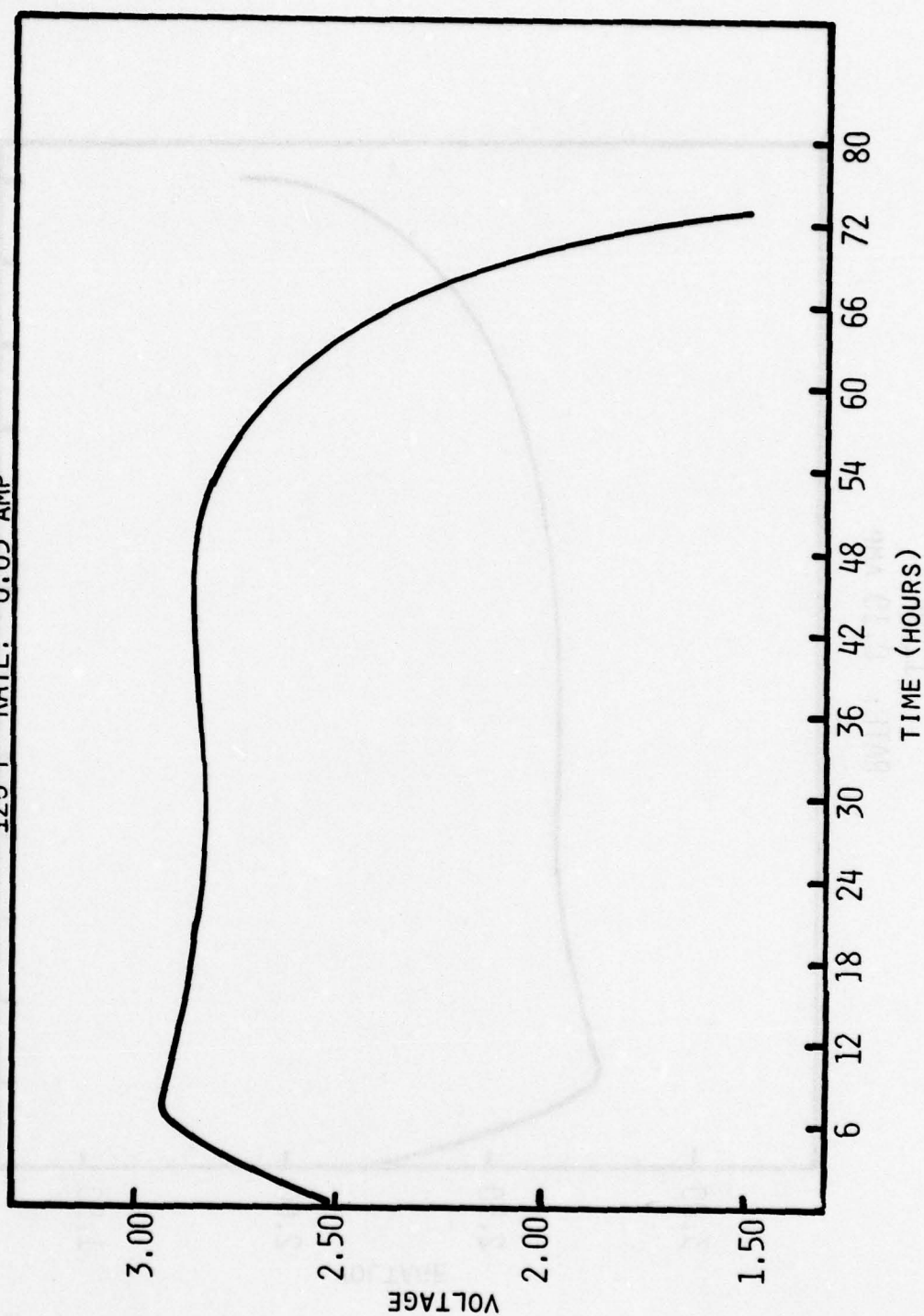FIGURE 17 Ca/SOCL$_2$ DISCHARGE CURVE 0°F - RATE: 1.00 AMP

-38-

FIGURE 18 CA/SOCL$_2$ DISCHARGE CURVE 120°F - RATE: 0.05 AMP

CA/SOCL$_2$
DISCHARGE CURVE
120°F
RATE: 0.10 AMP

FIGURE 19 CA/SOCL$_2$ DISCHARGE CURVE 120°F - RATE: 0.10 AMP

VOLTAGE

TIME (HOURS)

-40-

Ca/SOCl$_2$
DISCHARGE CURVE
120°F
RATE: 0.50 AMP

TEMPERATURE (°F)

VOLTAGE

0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
TIME (HOURS)

3.00
2.50
2.00
1.50

FIGURE 20 CA/SOCL$_2$ DISCHARGE CURVE 120°F – RATE: 0.50 AMP

FIGURE 21 CA/SOCL$_2$ DISCHARGE CURVE 120°F - RATE: 1.00 AMP

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electrolyte, causing a hydraulic vent when heated to 180°F. Cells with reduced electrolyte volume also vented at 180°F, and venting at a higher temperature was noted during 165°F discharges. More will be said about this type of vent in the section in abuse tests.

Cell discharges at 165°F are shown in Figures 22 -25. Cell capacity at the 50 ma rate was reduced below that of any other temperature except -20°F, producing 2.9AH. As was the case at 120°F, 165°F discharge could be completed only at rates up to 500 ma. Cells discharged at 1000 ma vented from overheating at approximately 1.5 hours and a temperature on the side of the cell case of 190°F. The vent was the same mild occurance noted above and was detected only by its odor.

Teardown of 120° and 165°F discharged cells revealed the same thick gray film noted at 0° and -20°F, but which has always been absent at 75°F. In all cases the heaviest film occured at -20° and 165°F.

The same system components were also evaluated in larger rectangular cells, originally intended to yield 25AH. The cells were made using the same electrolyte solutions as previously discussed cells. Cathode size was 3.5" x 1.75" x .017", with sixteen (16) cathodes per cell. Anodes were pure Ca foil on expanded Ni grid and were .013" thick. The overall dimensions of the case were 4.00" x 2.00" x0.85". Two terminals were used and the case was allowed to float. A single vent was incorporated into the cover.

The cells were discharged at lower rates than the "half-D" cells; 50 ma, 100 ma, 500 ma and 1000 ma, corresponding to 0.04, 0.079, 0.396, and 0.791 ma/cm^2 respectively. Discharge curves are shown in Figures 26 - 30. A summary of the effects of discharge rate on capacity is given in Figure 26. Although the cell capacity was originally projected
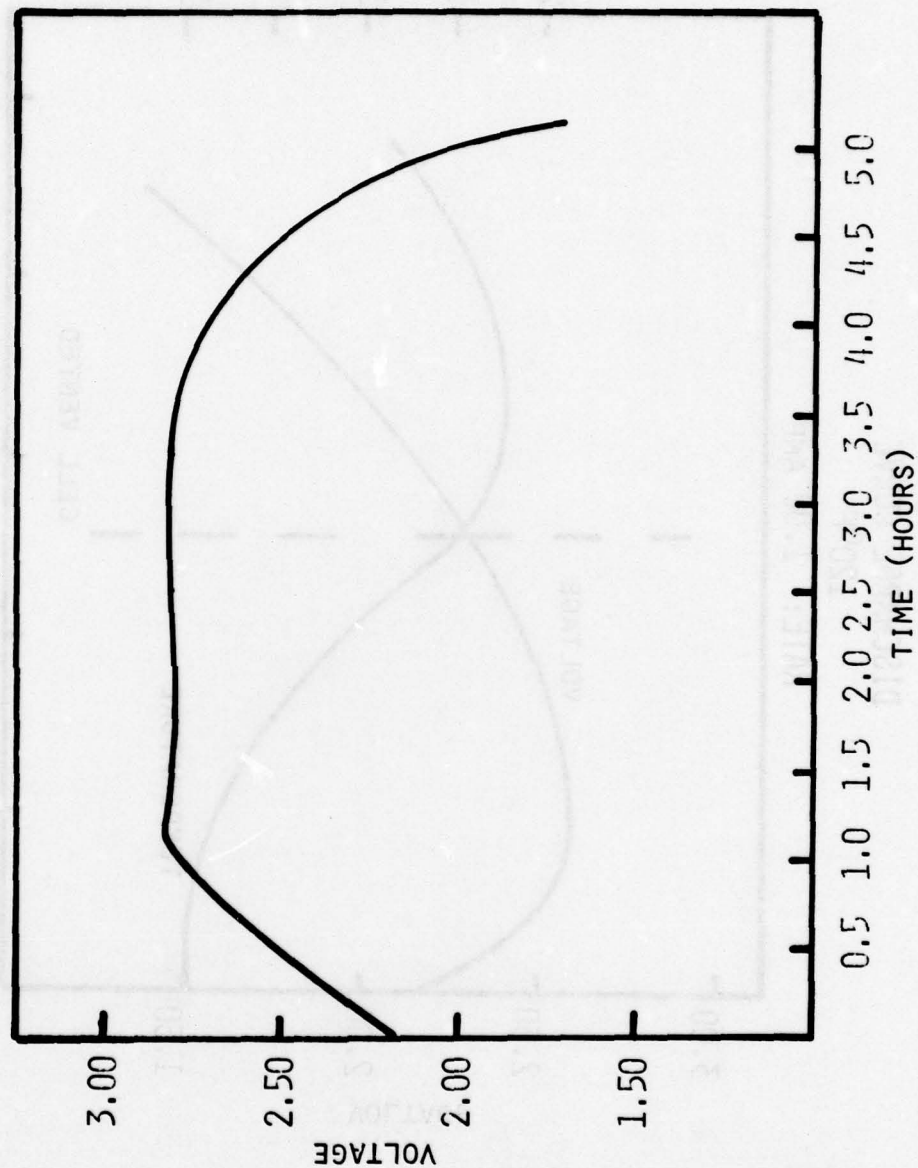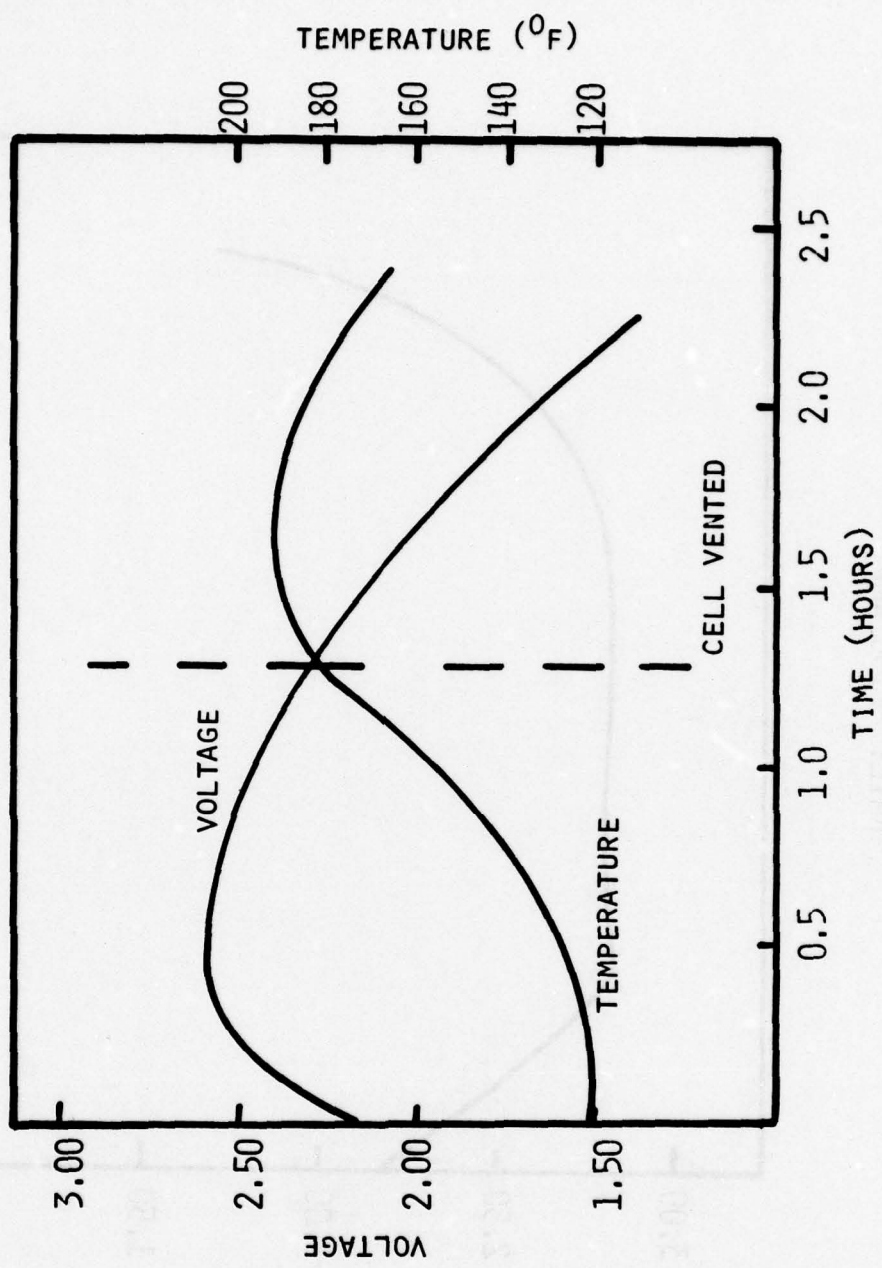
-43-

FIGURE 22 Ca/SOCl$_2$ DISCHARGE CURVE 165°F - RATE: 0.05 AMP

Ca/SOCl₂
DISCHARGE CURVE
165°F
RATE: 0.010 AMP
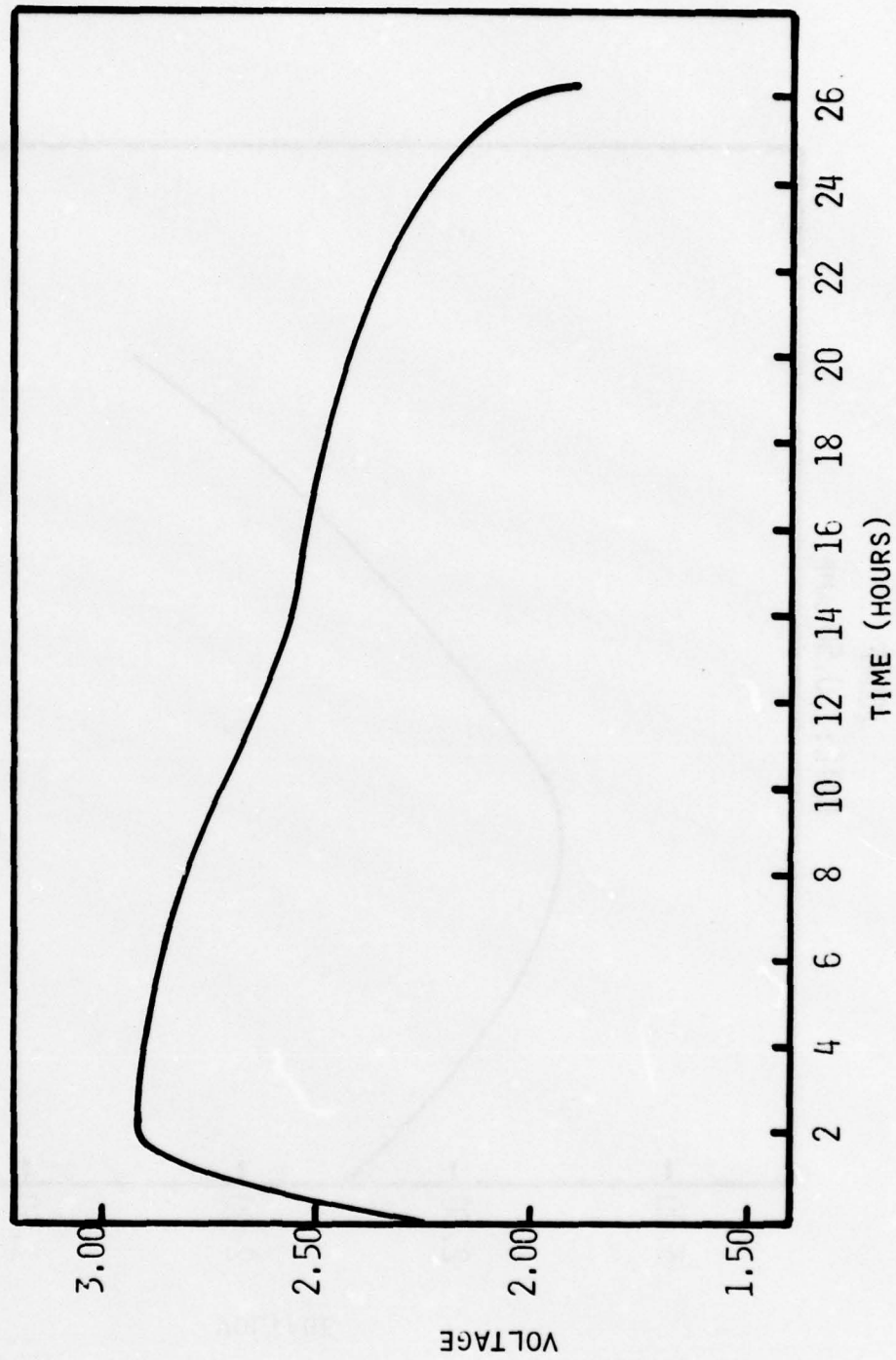
FIGURE 23 CA/SOCL₂ DISCHARGE CURVE 165°F - RATE: 0.10 AMP

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Ca/SOCL$_2$
DISCHARGE CURVE
165°F
RATE: 0.50 AMP

VOLTAGE

3.00

2.50

2.00

1.50

0.5 1.0 1.5 2.0 2.5

TIME (HOURS)
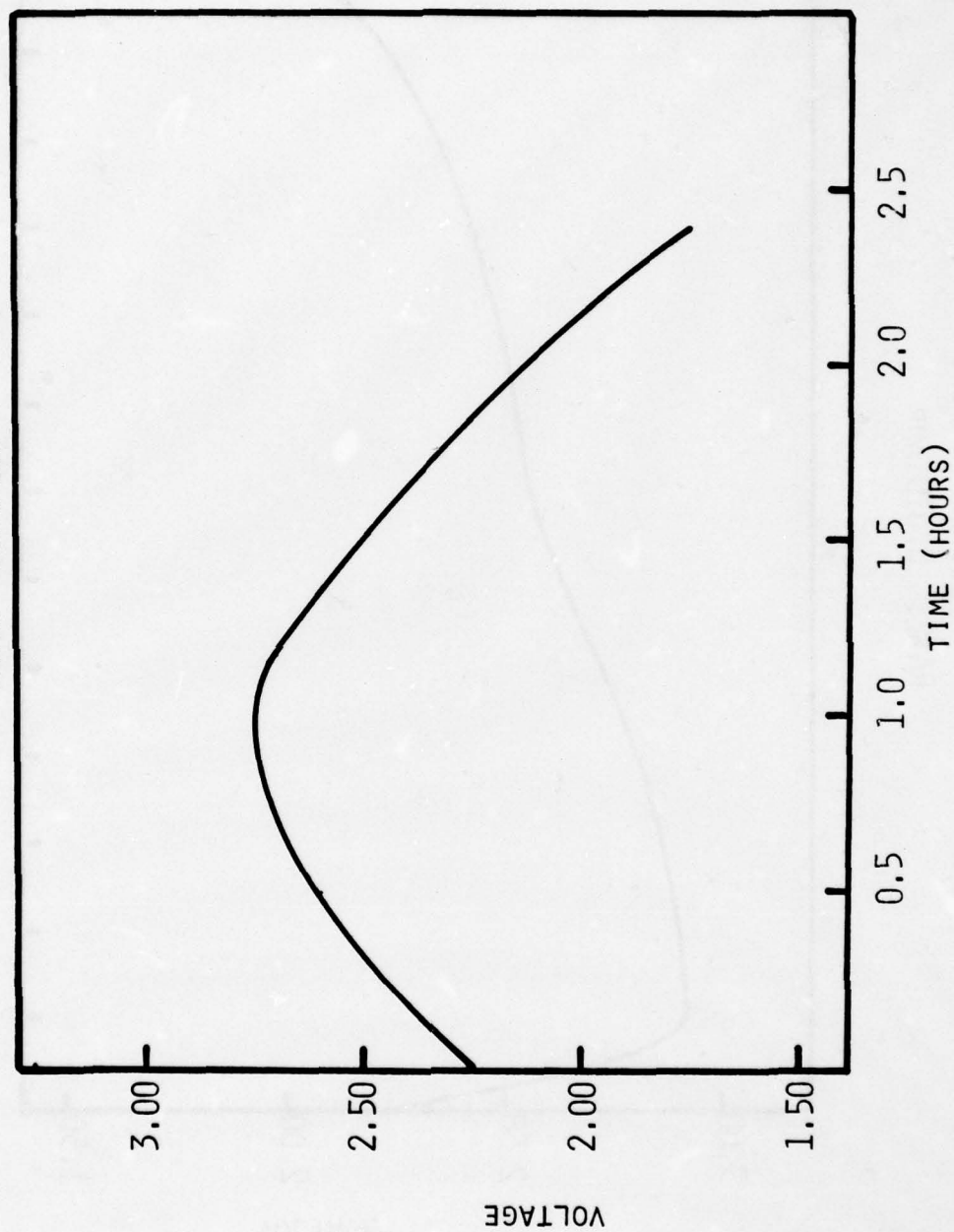
FIGURE 24 CA/SOCL$_2$ DISCHARGE CURVE 165°F – RATE: 0.50 AMP
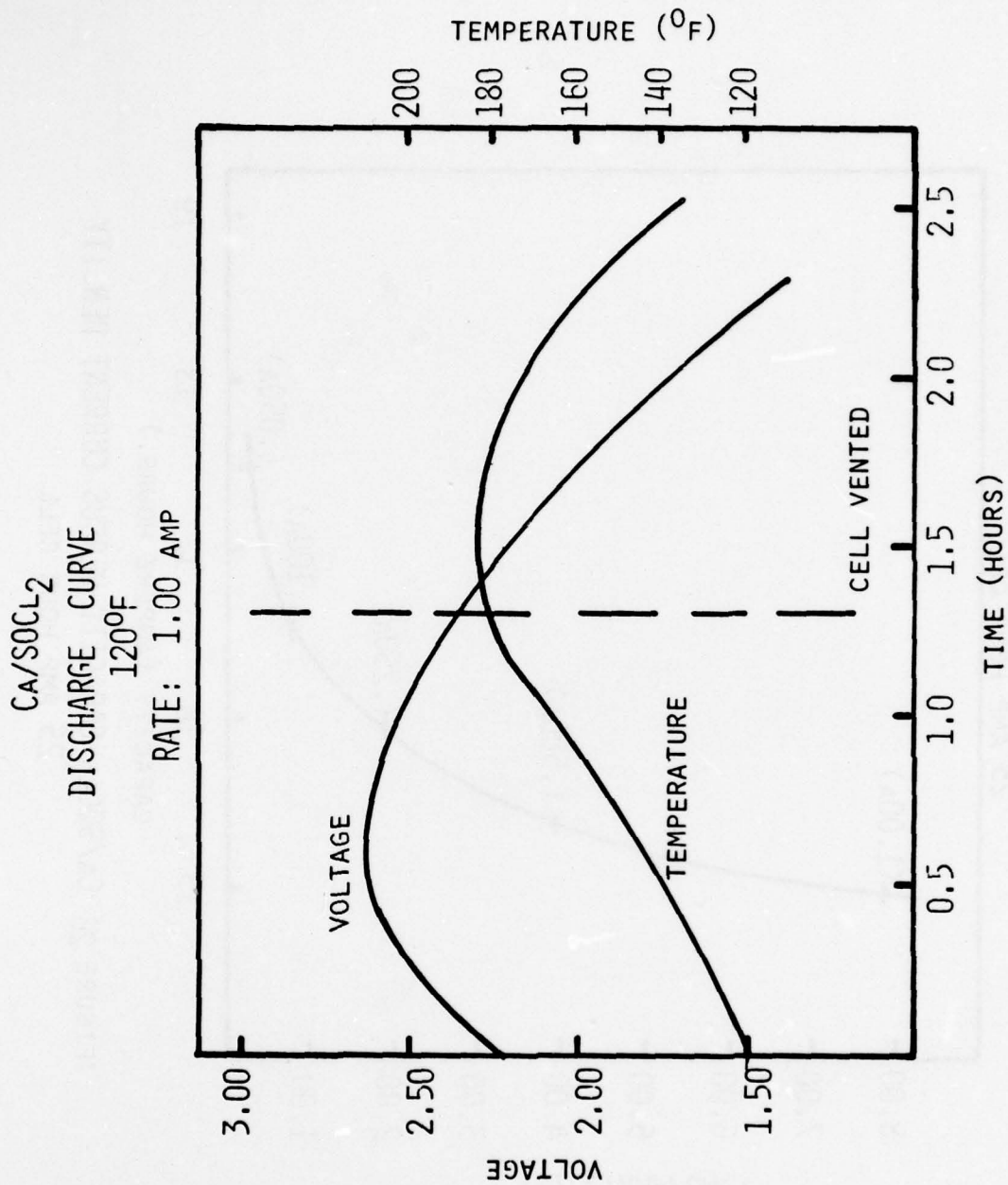
FIGURE 25 Ca/SOCL₂ DISCHARGE CURVE 120°F - RATE: 1.00 AMP

CA/SOCL$_2$

CAPACITY VERSUS CURRENT DENSITY
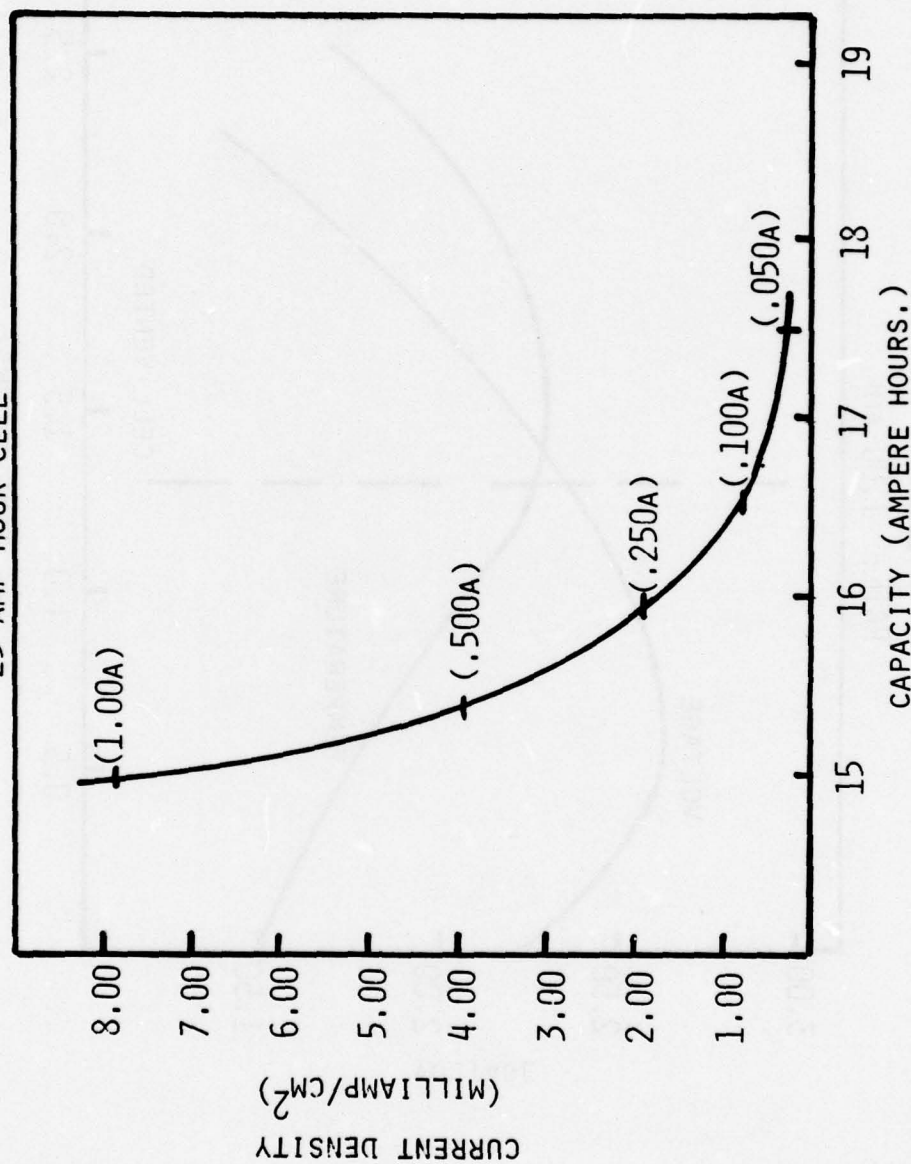
25 AMP HOUR CELL

FIGURE 26 CA/SOCL$_2$ CAPACITY VERSUS CURRENT DENSITY
25 AMP HOUR CELL

Ca/SOCL$_2$
DISCHARGE CURVE
25 AMP HOUR CELL S/N 17
RATE: 0.050 AMP STANDARD STACK
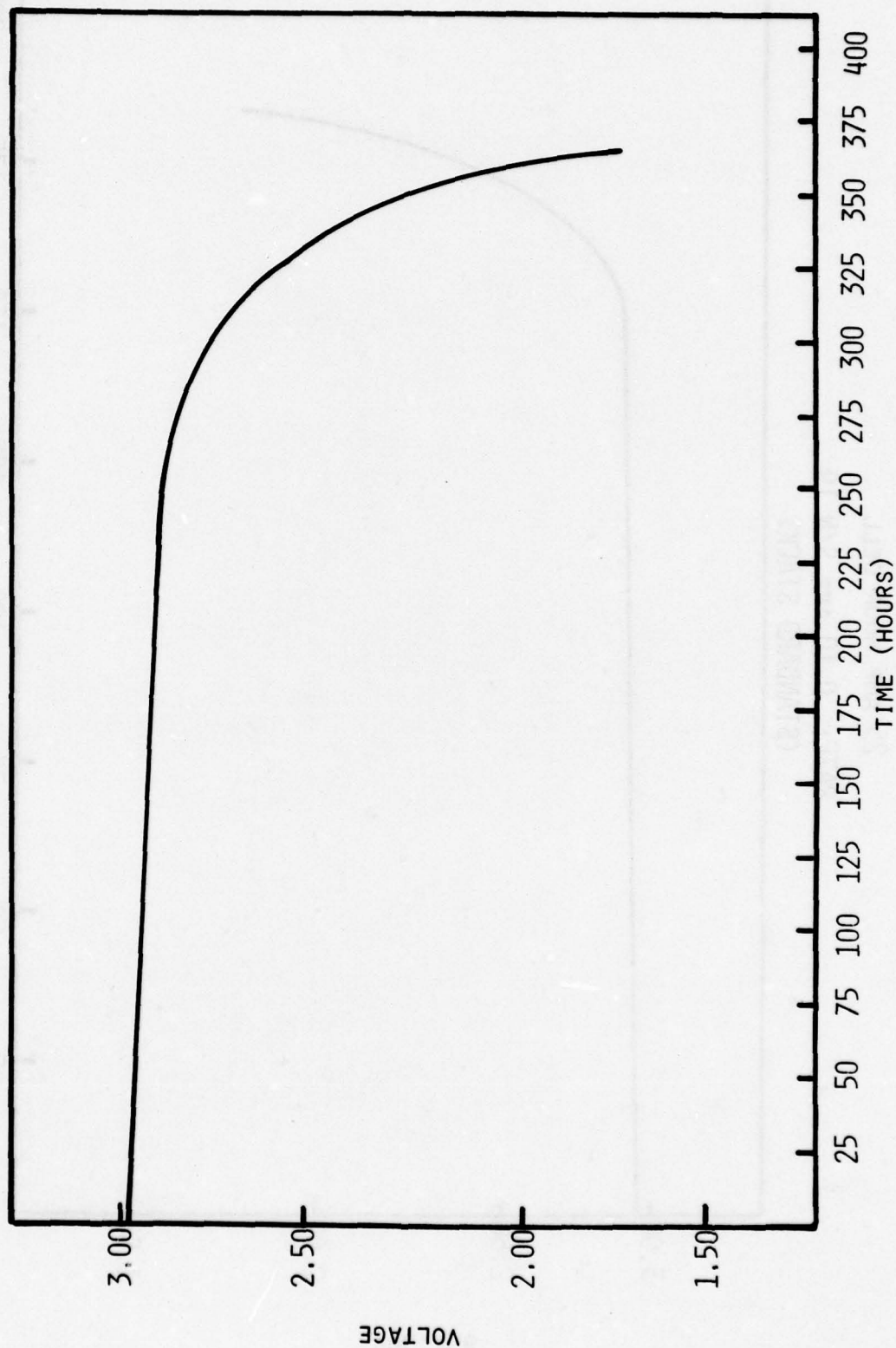
FIGURE 27 Ca/SOCL$_2$ DISCHARGE CURVE 25 AMP HOUR CELL S/N 17 - RATE: 0.050 AMP

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CA/SOCL$_2$

DISCHARGE CURVE

25 AMP HOUR CELL

RATE: 0.10 AMP S/N 19

(STANDARD STACK)

VOLTAGE

TIME (HOURS)
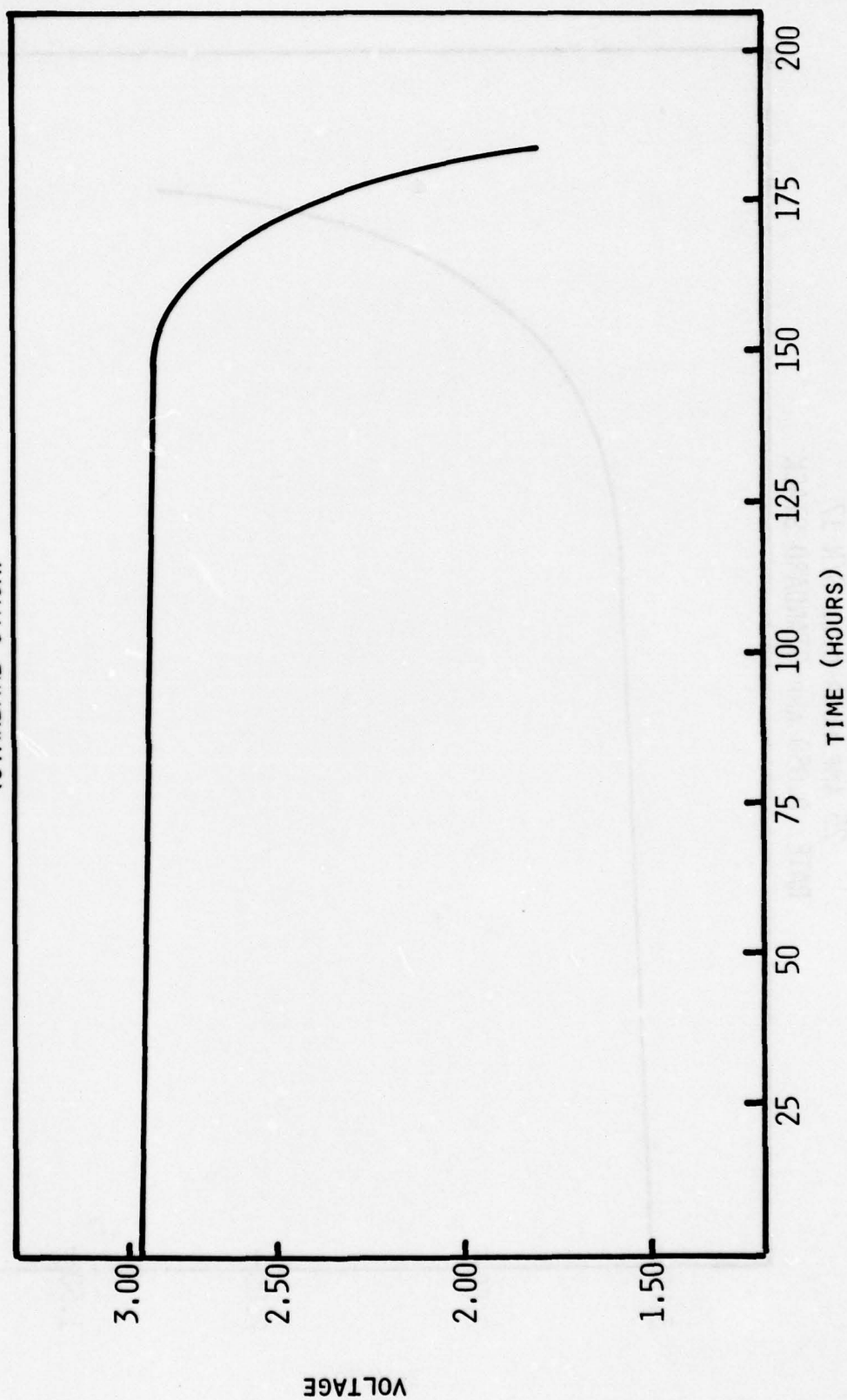
FIGURE 28 CA/SOCL$_2$ DISCHARGE CURVE 25 AMP HOUR CELL–RATE: 0.10 AMP S/N 19

CA/SOCL$_2$

DISCHARGE CURVE

25 AMP HOUR CELL

RATE: .050 AMP S/N 86

(STANDARD STACK)

FIGURE 29 CA/SOCL$_2$ DISCHARGE CURVE 25 AMP HOUR CELL-RATE: 0.5 AMP S/N 36

Ca/SOCL$_2$
DISCHARGE CURVE
25 AMP HOUR CELL
RATE: 1.00 AMP S/N 11

STANDARD STACK

VOLTAGE

3.00

2.50

2.00

1.50

2   4   6   8   10   12   14

TIME (HOURS)

FIGURE 30 CA/SOCL$_2$ DISCHARGE CURVE 25 AMP HOUR CELL-RATE: 1.00 AMP S/N 11 (STANDARD STACK)

to be 25 AH, actual capacity realized was 17.5 AH at 0.04 ma/cm^2 and
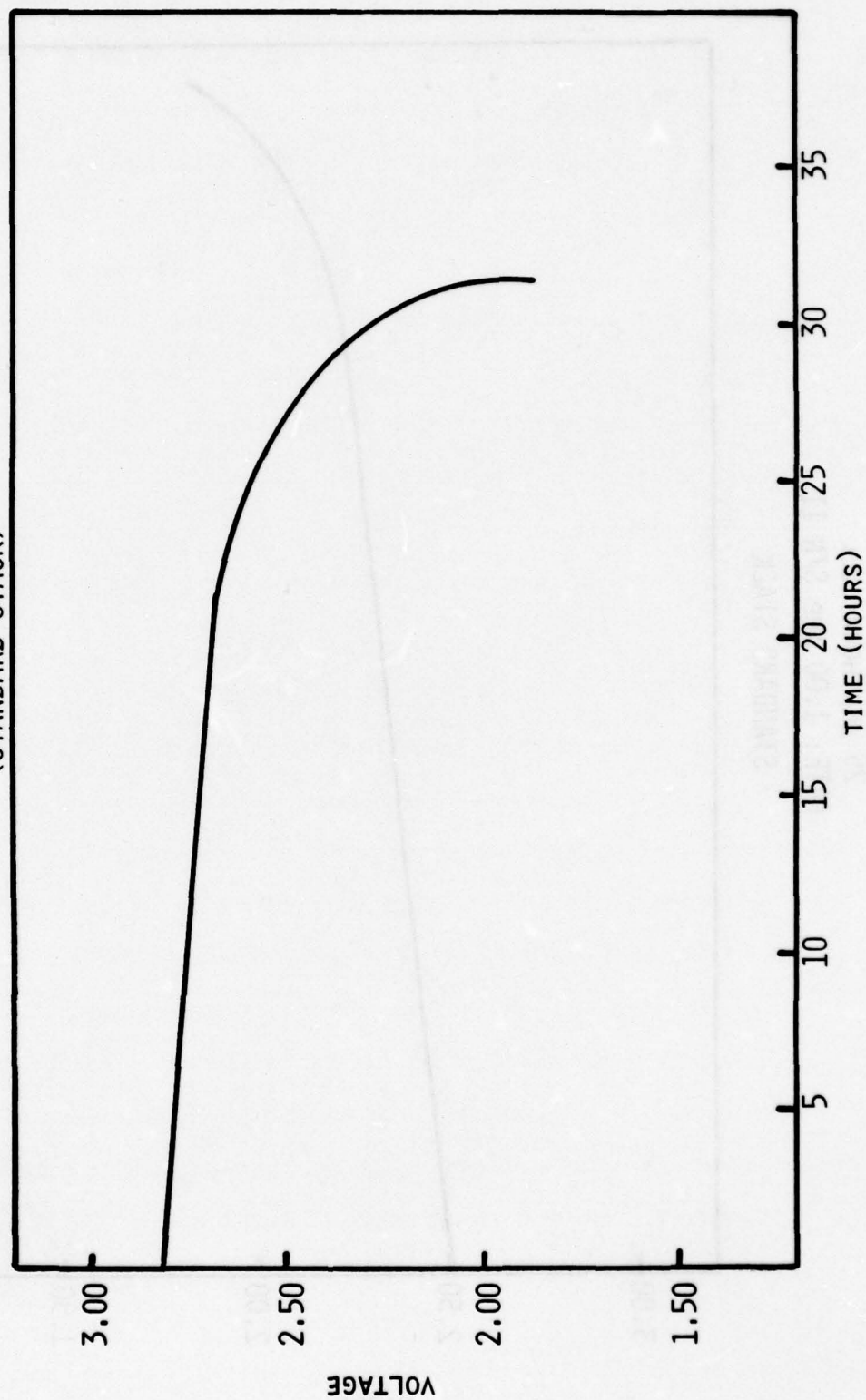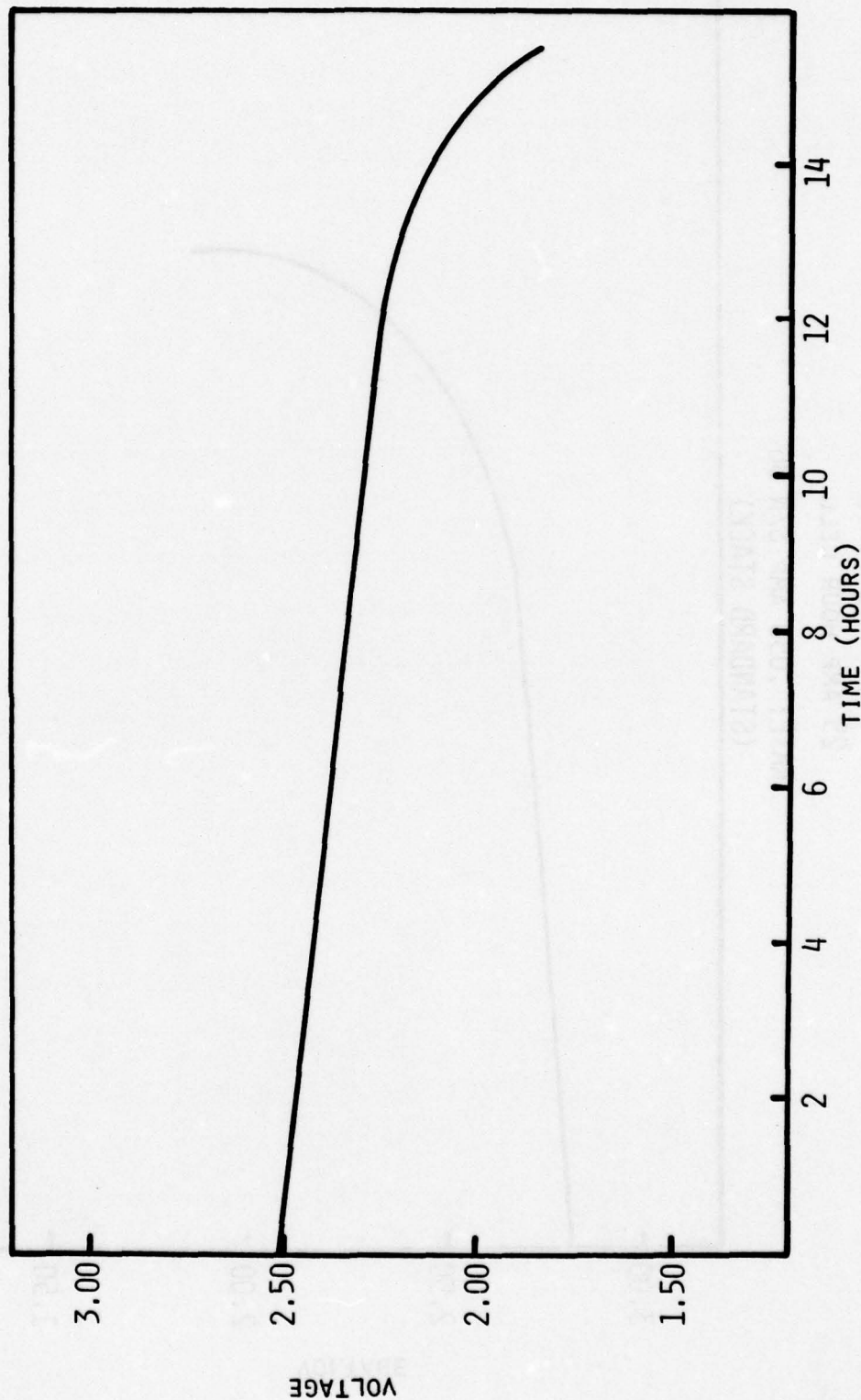
15.0 AH at .0791 ma/cm^2, all at 75^{o}F. Teardown of the cells following

discharge revealed the grayish film noted previously on the anode sur-

face; however, this was the first time the film was noted on a cell

discharged at room temperature. The rest of the cell appeared normal

except that the cell appeared to be too dry, and cathode expansion was

more severe than expected.

A second group of cells was prepared having only twelve (12) cathodes,

made with the same components previously used in the sixteen (16) plate

cell. The resulting cell stack was much looser. Discharge of cells pro-

duced the same capacities as before, an increase in the electrode effic-

iency of 25%. Upon teardown, the same gray film was in evidence but to

a lesser extent and much more residual electrolyte was remaining.

SECTION IV

STORAGE EVALUATION

One of the efforts occurring in both phases of this work is an eight-

teen (18) month storage test to be conducted on a standard Ca/SOCl$_2$ cell

at 25 and 55^{o}C. The cell used for the test was the "half-D" cell previously

discussed. The test was originally planned to start four (4) months before

the end of Phase I and continue fourteen (14) months into Phase II. The test

was not actually started, however, until the last month of the first phase .

A six (6) month 75^{o}F storage test was conducted on a group of fifteen

(15) cells earlier in Phase I which has been completed. Cells were removed

from storage at one (1), three (3) and six (6) months, pulsed at 100 ma using a

a recording oscillograph, and then discharged at a constant 100 ma at 75^{o}F.

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The cell impedance was measured prior to pulsing with a Hewlett Packard

1 KHz AC millohmeter. The results of this test are given in Table 8.

TABLE 8

PRELIMINARY STORAGE CELLS DISCHARGE DATA

Time In Storage	S/N	Open Circuit (Volts)	Rise Time To 2.00 (Seconds)	Impedance (Ohms)	Rate (Amps)	Capacity (Ampere Hours)
1 Month	26	3.10	1	.950	.1	3.50
1 Month	27	3.12	1	.900	.1	3.46
3 Months	28	3.10	1	1.80	.1	3.40
3 Months	29	3.09	1	1.75	.1	3.42
6 Months	30	3.10	2	2.30	.1	3.45
6 Months	31	3.10	2	2.35	.1	3.40

The greatest change observed as storage progressed was in the cell impedance

as measured with the AC millohmeter. Impedance r o se from an average of 700

ohms to 2.35 ohms during the six (6) months. Delay time, defined for this

purpose as the time required for the cell voltage to rise above 2.0 volts

after loading, increased from zero to approximately two seconds. Fresh cells,

when loaded at the same 100 ma, dropped from OC to only 2.75 volts, then re-

covered to 2.96 volts within one (1) second. The absolute time noted for

voltage delay cannot be assumed indicative of cell performance after a com-

plete uninterrupted stand as the cells were pulsed at 100 ma for five (5)

seconds each month. A plot of the change in initial load voltage, imped-

ance, and voltage delay for the characteristic cell during the six (6)

months is given in Figure 31.. Despite the rise in impedance during the

storage period, the capacity at a 100 ma constant rate remained nearly

constant at 3.4 to 3.5 AH for the duration of the six (6) month test.

The eighteen (18) month test has been in progress for only one (1)

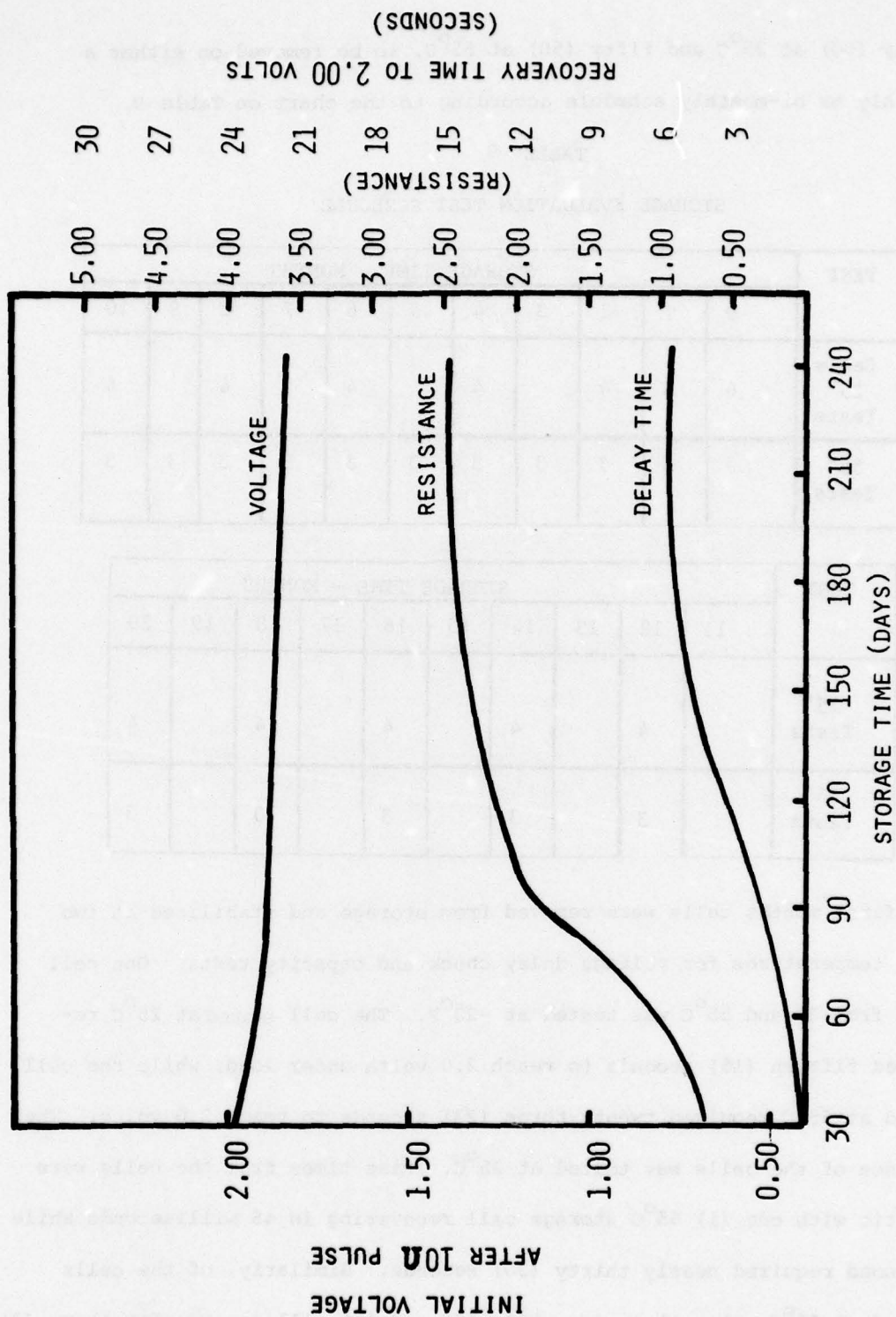month as of the writing of this report. One hundred cells have been stored,

FIGURE 31 CA/SOCL$_2$ VOLTAGE DELAY

-55-

fifty (50) at 25°C and fifty (50) at 55°C, to be removed on either a monthly or bi-monthly schedule according to the chart on Table 9.

TABLE 9

STORAGE EVALUATION TEST SCHEDULE

TEST	STORAGE TIME – MONTHS										
	0	1	2	3	4	5	6	7	8	9	10
Cells 25° Tests	6	4	4		4		4		4		4
55° Tests	5	3	3	3	3	3	3	3	3	3	3

TEST	STORAGE TIME – MONTHS									
	11	12	13	14	15	16	17	18	19	20
25° Tests		4		4		4		4		4
55° Tests		3		3		3		3		3

The first months cells were removed from storage and stabilized at two test temperatures for voltage delay check and capacity tests. One cell each from 25 and 55°C was tested at -20°F. The cell stored at 25°C required fifteen (15) seconds to reach 2.0 volts under load, while the cell stand at 55°C required twenty-three (23) seconds to reach 2.0 volts. The balance of the cells was tested at 25°C. Rise times from the cells were erratic with one (1) 55°C storage cell recovering in 45 milliseconds while a second required nearly thirty (30) seconds. Similarly, of the cells stored at 25°C, rise times were 120, 180 and 120 milliseconds for three (3) cells. The cells had not been fully discharged for capacity test as of this writing; however all will be discharged at 100 ma constant load.

SECTION V

SAFETY EVALUATION

One of the original incentives for this program was the desire
for a high energy cell which could tolerate extreme abuse without the
hazardous response sometimes noted in $Li/SOCl_2$ cells. Due to the rela-
tively unknown characteristics of $Ca/SOCl_2$ and the possibility of un-
forseen hazards, several simple abuse tests were made at the start of
the program, using the first sealed "half-D" cells fabricated. The
tests run were short circuit and overheating. The short circuit tests
were done very simply without monitoring any cell parameters. A copper
strap was placed across the terminals and the cell was observed to note
if and after what time interval anything happened. Of six (6) cells
tested in this manner at an ambient temperature of $60^{\circ}F$, none were
observed to vent. All cells remained sealed and there was no evidence
of electrolyte leakage. An additional six (6) cells were subjected to
an overheating test whereby a propane torch was placed with the flame
touching the side of the cell case. In five (5) of the six (6) tests,
the cells were observed to vent quietly followed by a substantial emis-
sion of a white vapor for several seconds with no evidence of flame.
One cell however, vented violently, and was moved several feet by the
force of the vent. This result was not consistant with the other eleven
(11) cells tested. Further, in view of the subsequent tests of several
hundred cells which will be discussed, the results would appear even more
inconsistant for a $Ca/SOCl_2$ cell. It has been suggested, but cannot be
confirmed, that the maverick cell which vented so violently was not a
$Ca/SOCl_2$ cell, but rather was a $Li/SOCl_2$ cell, many of which were made at

that same time in the same "half-D" cases and discharged along with
$Ca/SOCl_2$ cells.

No further abuse tests were done during most of the reporting period
and several hundred cells were made and tested without incident. The
last work conducted in Phase I was a complete abuse test carried out on
approximately one-hundred fifty (150) cells.

The tests conducted were: a) Short Circuit

b) Incineration

c) Reversal

d) Charging

e) Shock

f) Vibration

g) Crushing

h) Puncture

Certain of the tests were preformed using cells in various states of
discharge. The methods and results of each test are given as follows:

a) Short Circuit - The short circuit test was made by shorting the
cell leads through a 50a/100mv shunt. The voltage of the cell was moni-
tored continuously as well as the temperature on the side of the cell case.
The cells were tested at outside ambient temperature which ranged from
$60-80^{\circ}F$. All cell voltages dropped immediately to approximately 100mv
after shorting. The initial short circuit currents were about 5A, rising
to 15-17A peak within one to two minutes. Cells vented during the same
one to two minute period, the current usually peaking quickly within 10 -20
seconds following the vent. Skin temperature usually continued to rise for
several minutes after venting and peaked out at $160-180^{\circ}F$ before falling

back to outside ambient temperature in about fifteen minutes. Cell venting was always very mild, often inaudible and accompanied by little $SOCl_2$ as a liquid or vapor. No deformation of the case was noted, and the unrestrained cell was not moved by the venting. A plot of a typical short circuit showing voltage, current and temperature is given in Figure 32

b) Incineration - The incineration test was not a true incineration but more of an overheating test. The cells were placed on their side with a propane flame on the cell side, half way down the cell. The tests were made using fresh cells; cells partially discharged at $75^{\circ}F$; and cells partially discharged at $-20^{\circ}F$. Upon contact with the flame, the side of the case turned dull red and the cell vented at approximately 1.5 minutes, evidenced by a white spray from the vent opening. The torch was left on the cell for a minimum of five minutes after the vent, but produced no further results. There was no noticeable difference in the results of different test samples.

Following the test, the samples were examined and several were found to have small holes in the side of the case where the flame had touched. Since the white $SOCl_2$ spray only came from the vent hole and not from the flame area, it was assumed that the hole was burned open after venting. At no time during the tests were any results other than mild venting noted. The cells were unrestrained but did not move during venting. No flame was ever noted; however, the propane flame was placed such that it would not likely ignite the normal vented products.

c) Reversal - The reversal test was performed on cells which had been discharged at the 50 ma rate to less than 0.1 volts, then reversed at a constant rate of .25 amps. The voltage was allowed to increase to maintain the
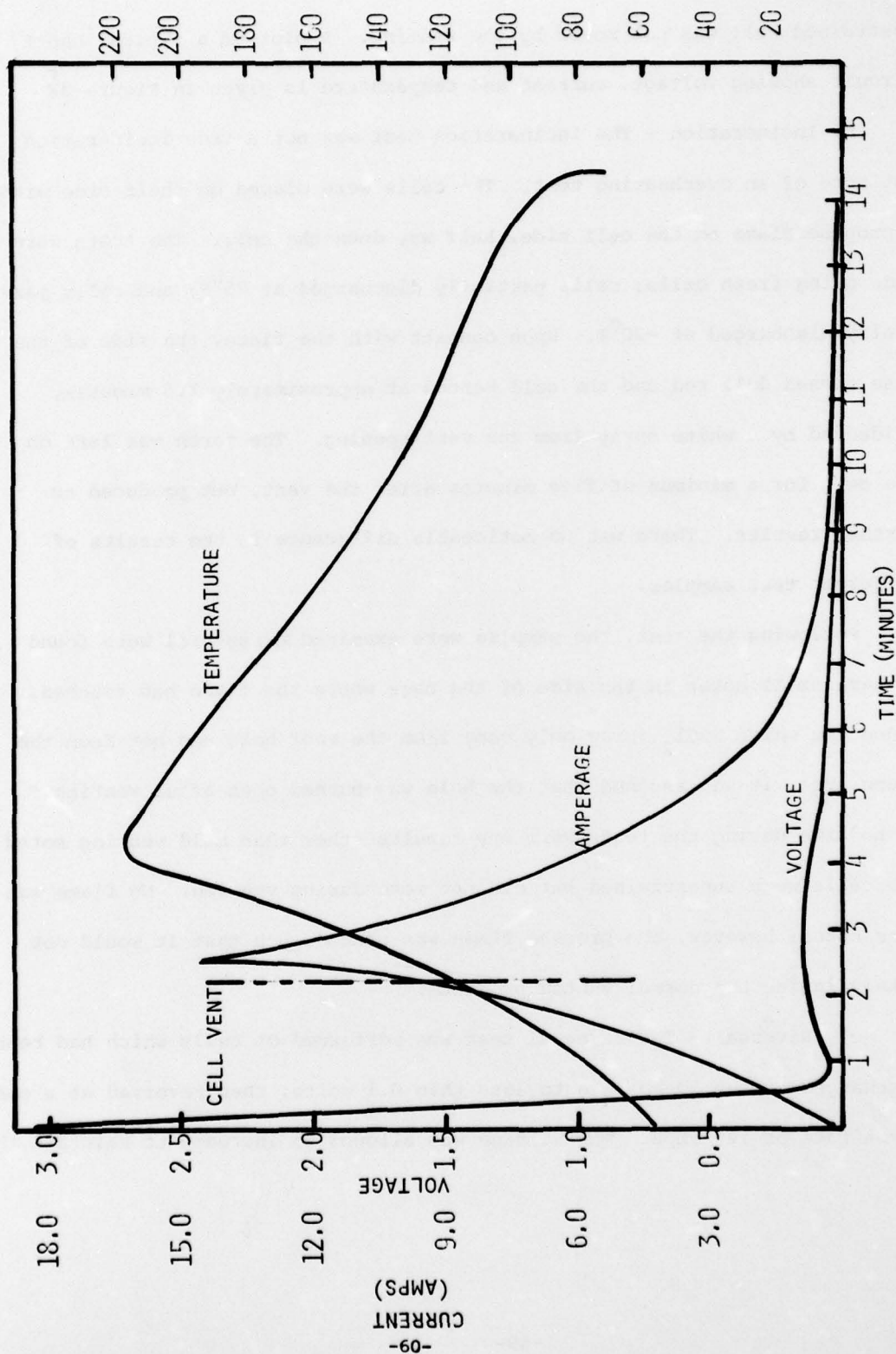
FIGURE 32 CA/SOCL$_2$ SHORT CIRCUIT

CA/SOCL$_2$

SHORT CIRCUIT

.25 amp rate up to negative 20 volts. The cells were insulated to reduce
heat losses during the test. A plot of a typical test is given in Figure
33. The initial voltage required to produce .25A current was -2.50. The
reversal was continued for 2.5 hours before reaching -20 volts where the
test was ended. The temperatures peaked out at approximately 160°F at 1.25
hours and dropped steadily afterwards. At no time during the test was there
any indication that venting had occurred; however, when the cell was removed
from the insulation after the test, the vent had opened slightly.

The remainder of the cells tested gave the same results, including
several which were power discharged and reversed at -20°F.

d) Charging - The charging test was done in two (2) sections, con-
stant current tests and constant potential tests. Test cells used in both
charging modes were prepared in five (5) conditions; fresh undischarged;
50% discharged at room temperature; 100% discharged at room temperature;
50% discharged at -20°F and 100% discharged at -20°F.

Constant current cells were charged at three rates, 50 ma, 100 ma and
1000 ma. None of the cells vented when charged to capacities of up to 16%
of normal cell capacity. Results from the three charging modes are shown
in Figures 34-36. The voltage required to sustain a 50 ma charge ranged
from 4.17 - 4.26 volts. Cell temperatures measured on the side of the cell
rose 8°F above ambient during the 7.5 hour test. Results at 100 ma were
similar except that the cell case temperature rose 24°F during the 3.5
hours of the test. The 1000 ma test required an initial charging potential
of 4.42 volts which dropped continuously to a minimum of 4.08 volts. The
test was continued until the temperature of the cell peaked and started
to fall. Total duration of the test was thirty-five minutes and skin temper-
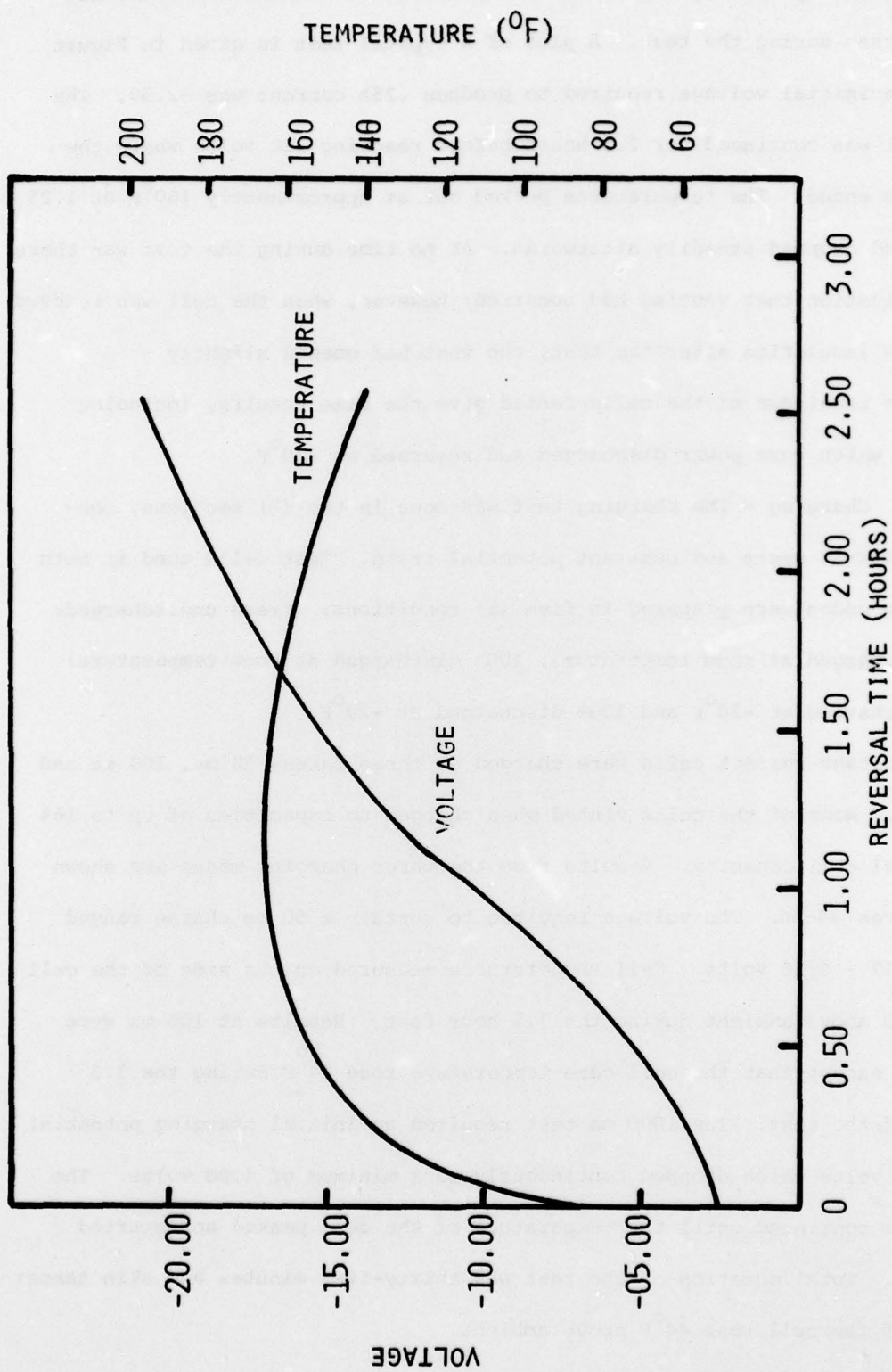ature of the cell rose 44°F above ambient.

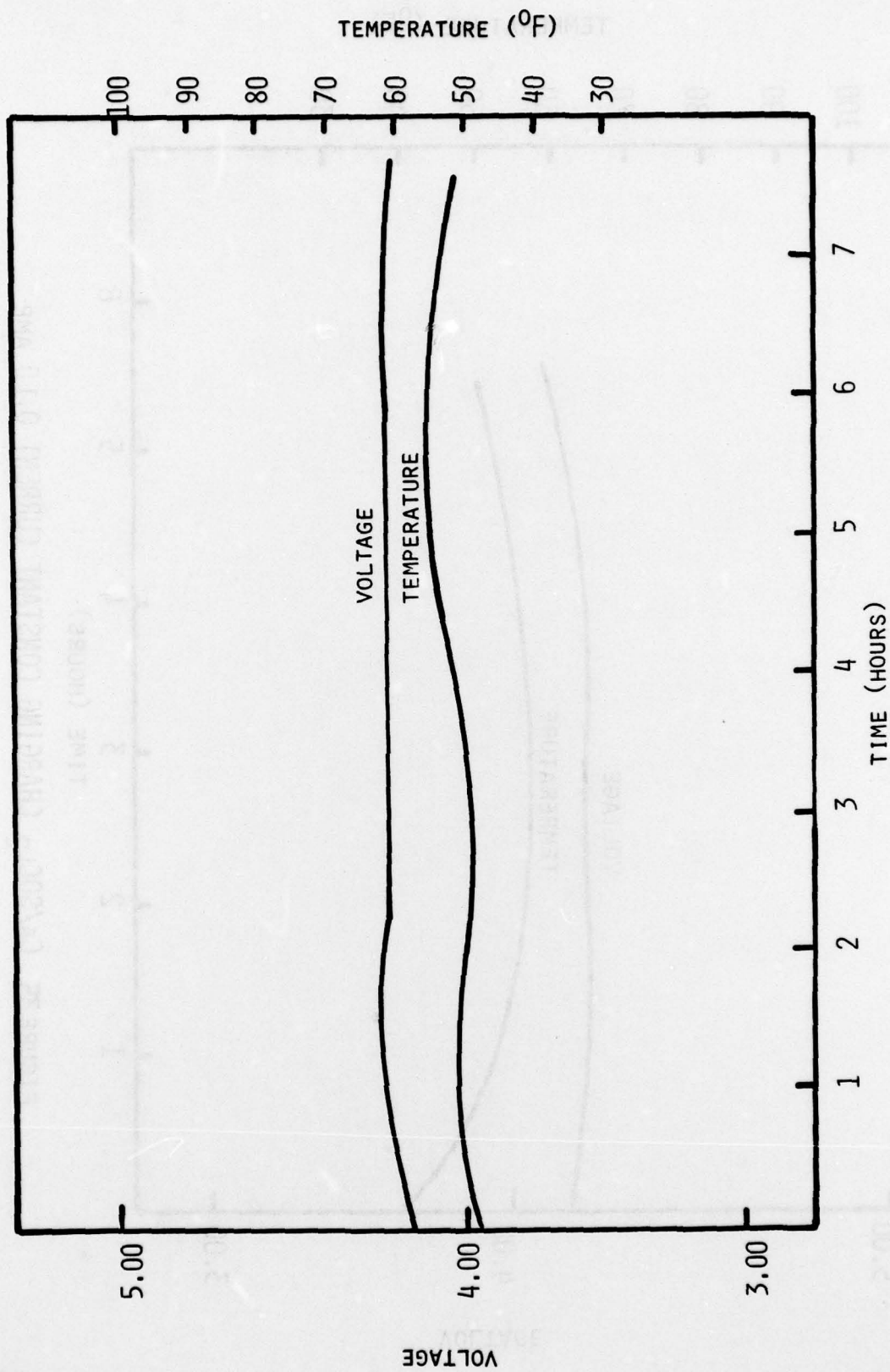FIGURE 33 CA/SOCL₂ CELL REVERSAL S/N 69 (FRESH CELL) 0.25 AMP.

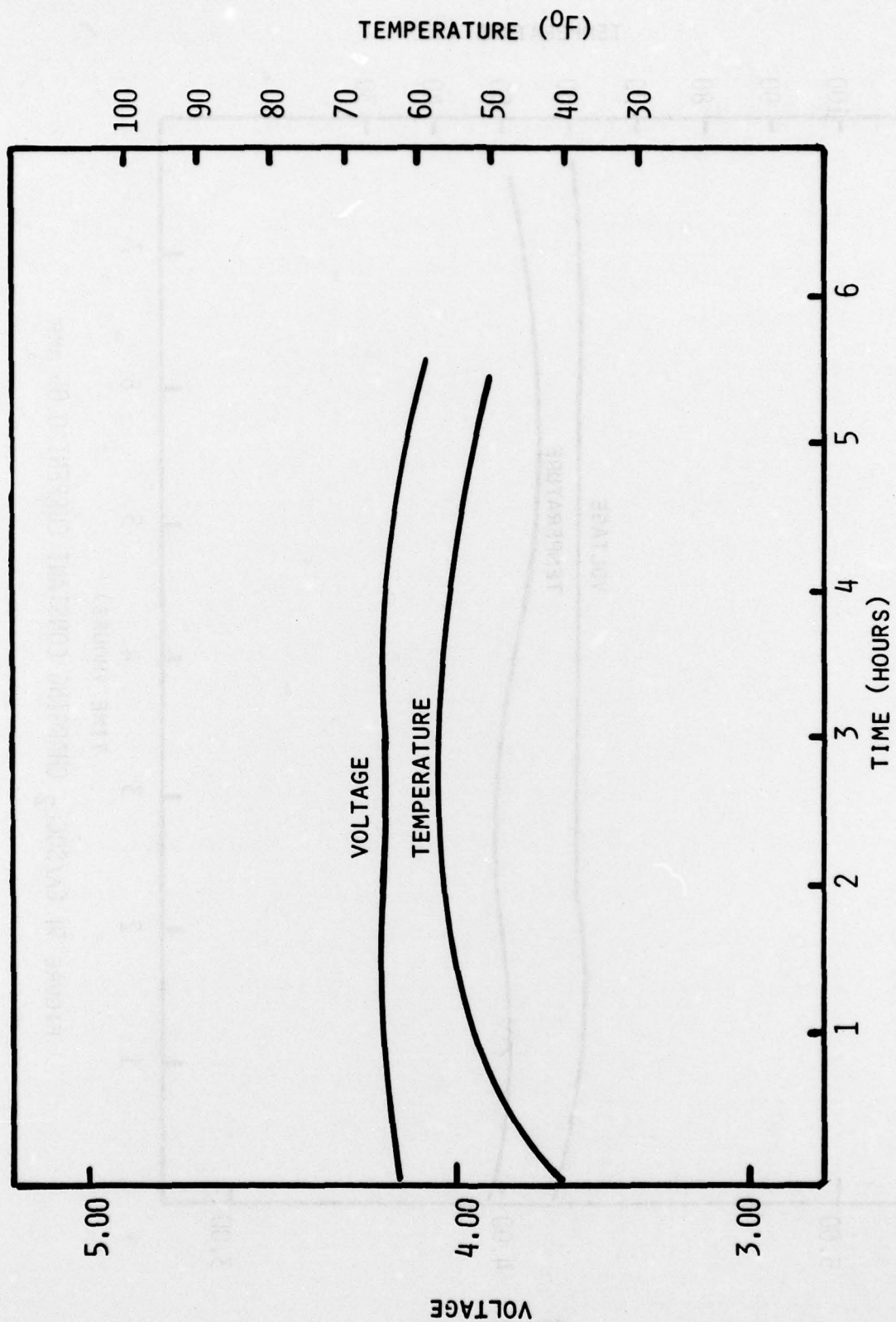FIGURE 34 CA/SOCL$_2$ CHARGING CONSTANT CURRENT 0.05 AMP

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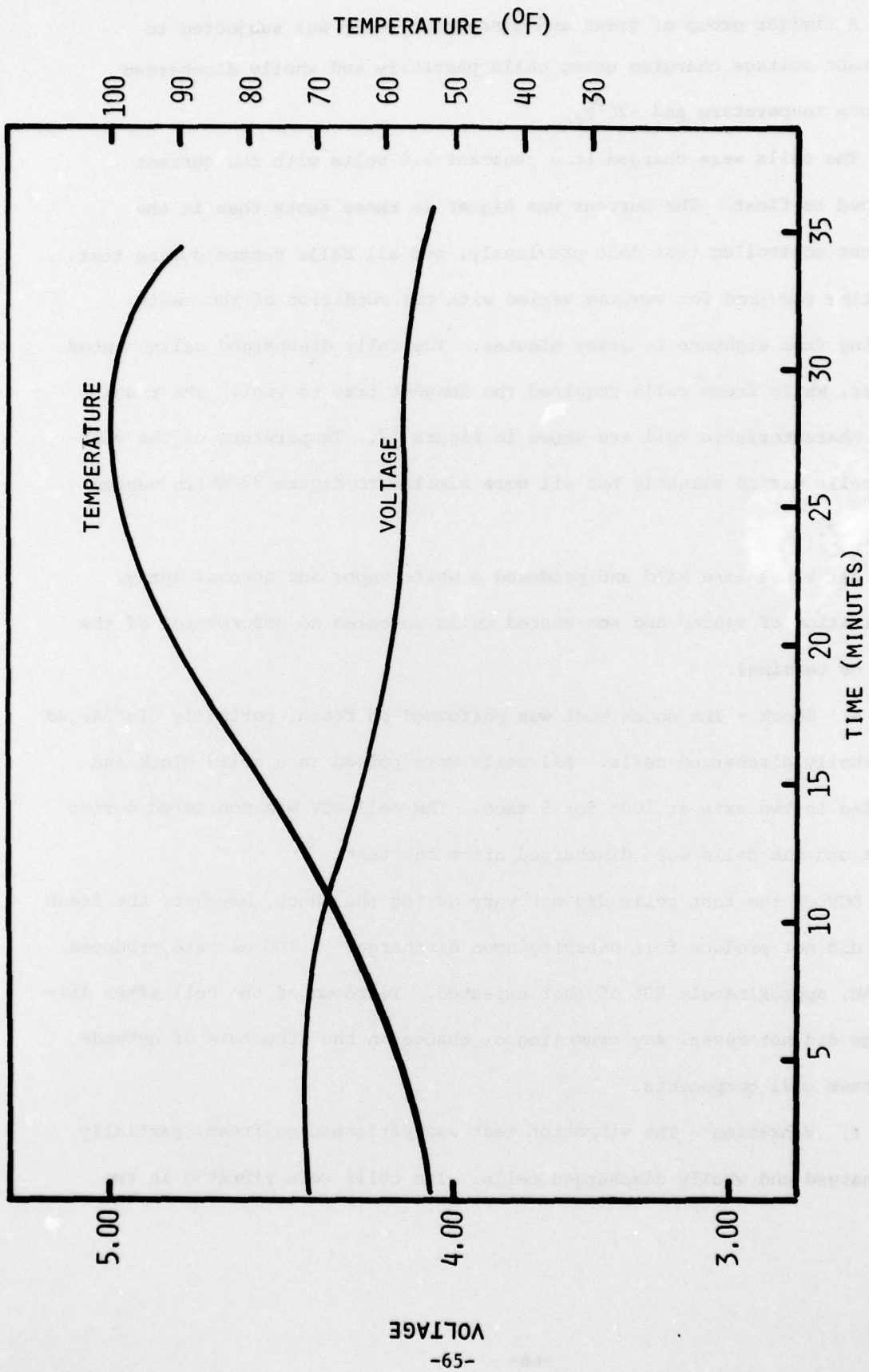FIGURE 35 CA/SOCL$_2$ CHARGING CONSTANT CURRENT 0.10 AMP

FIGURE 36 CA/SOCL₂ CHARGING CONSTANT CURRENT 1.00 AMP

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A similar group of fresh and discharged cells was subjected to constant voltage charging using cells partially and wholly discharged at room temperature and -20°F.

The cells were charged at a constant 5.0 volts with the current allowed to float. The current was higher in these tests than in the current controlled test done previously, and all cells vented during test. The time required for venting varied with the condition of the cells, ranging from eighteen to sixty minutes. The fully discharged cells vented sooner, while fresh cells required the longest time to vent. The results of a characteristic cell are shown in Figure 37. Temperature of the venting cells varied slightly but all were similar to Figure 37 which vented at 115°F.

All vents were mild and produced a white vapor and aerosal spray. Examination of vented and non-vented cells revealed no deformation of the case or terminal.

e) Shock - The shock test was performed on fresh, partially discharged and wholly discharged cells. All cells were potted in a solid block and shocked in two axis at 100g for 5 msec. The cell OCV was monitored during shock and the cells were discharged after the test.

OCV of the test cells did not vary during the shock, however, the fresh cell did not produce full capacity upon discharge. A 100 ma rate produced 2.6 AH, approximately 80% of that expected. Teardown of the cell after discharge did not reveal any crumbling or change in the structure of cathode or other cell components.

f) Vibration - The vibration test was performed on fresh, partially discharged and wholly discharged cells. The cells were vibrated in two

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TEMPERATURE (°F)

160
140
120
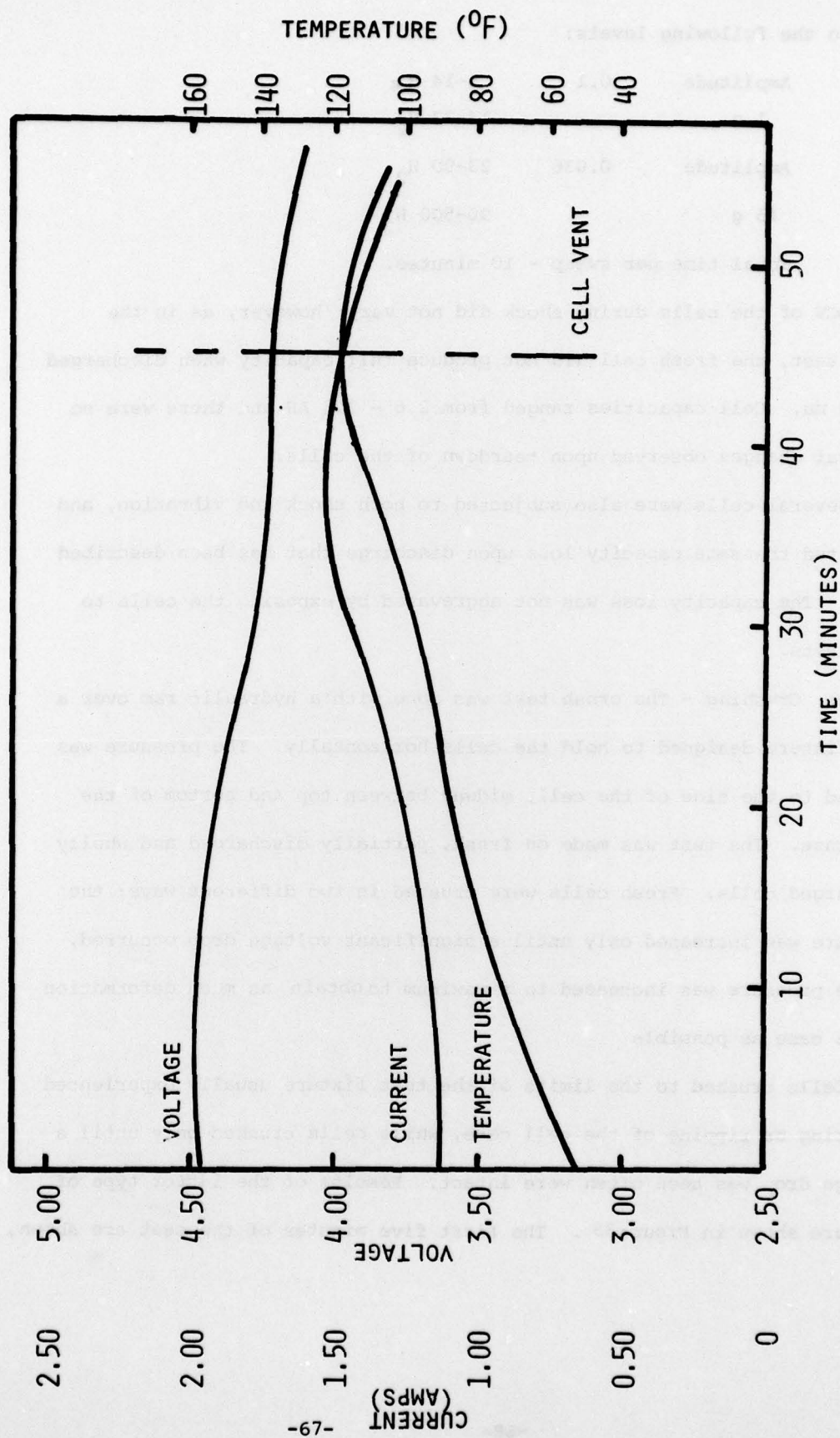100
80
60
40

CELL VENT

VOLTAGE

CURRENT

TEMPERATURE

5.00
4.50
4.00
3.50
3.00

VOLTAGE

2.50
2.00
1.50
1.00
0.50
0

CURRENT (AMPS)

0   10   20   30   40   50

TIME (MINUTES)

FIGURE 37 CA/SOCL$_2$ CONSTANT POTENTIAL CHARGING 5.00 VOLTS

axis to the following levels:

Amplitude	0.1	5-14 Hz
1 g		14-23 H_2
Amplitude	0.036	23-90 H_2
15 g		90-500 H_2

Total time per sweep - 10 minutes.

OCV of the cells during shock did not vary; however, as in the shock test, the fresh cell did not produce full capacity when discharged at 100 ma. Cell capacities ranged from 2.6 - 2.8 AH and there were no physical changes observed upon teardown of the cells.

Several cells were also subjected to both shock and vibration, and exhibited the same capacity loss upon discharge that has been described above. The capacity loss was not aggrevated by exposing the cells to both tests.

g) Crushing - The crush test was done with a hydraulic ram over a test fixture designed to hold the cells horizontally. The pressure was applied to the side of the cell, midway between top and bottom of the cell case. The test was made on fresh, partially discharged and wholly discharged cells. Fresh cells were crushed in two different ways; the pressure was increased only until a significant voltage drop occurred, or the pressure was increased to a maximum to obtain as much deformation of the case as possible

Cells crushed to the limits of the test fixture usually experienced a tearing or ripping of the cell case, while cells crushed only until a voltage drop was seen often were intact. Results of the latter type of test are shown in Figure 38 . The first five minutes of the test are shown,
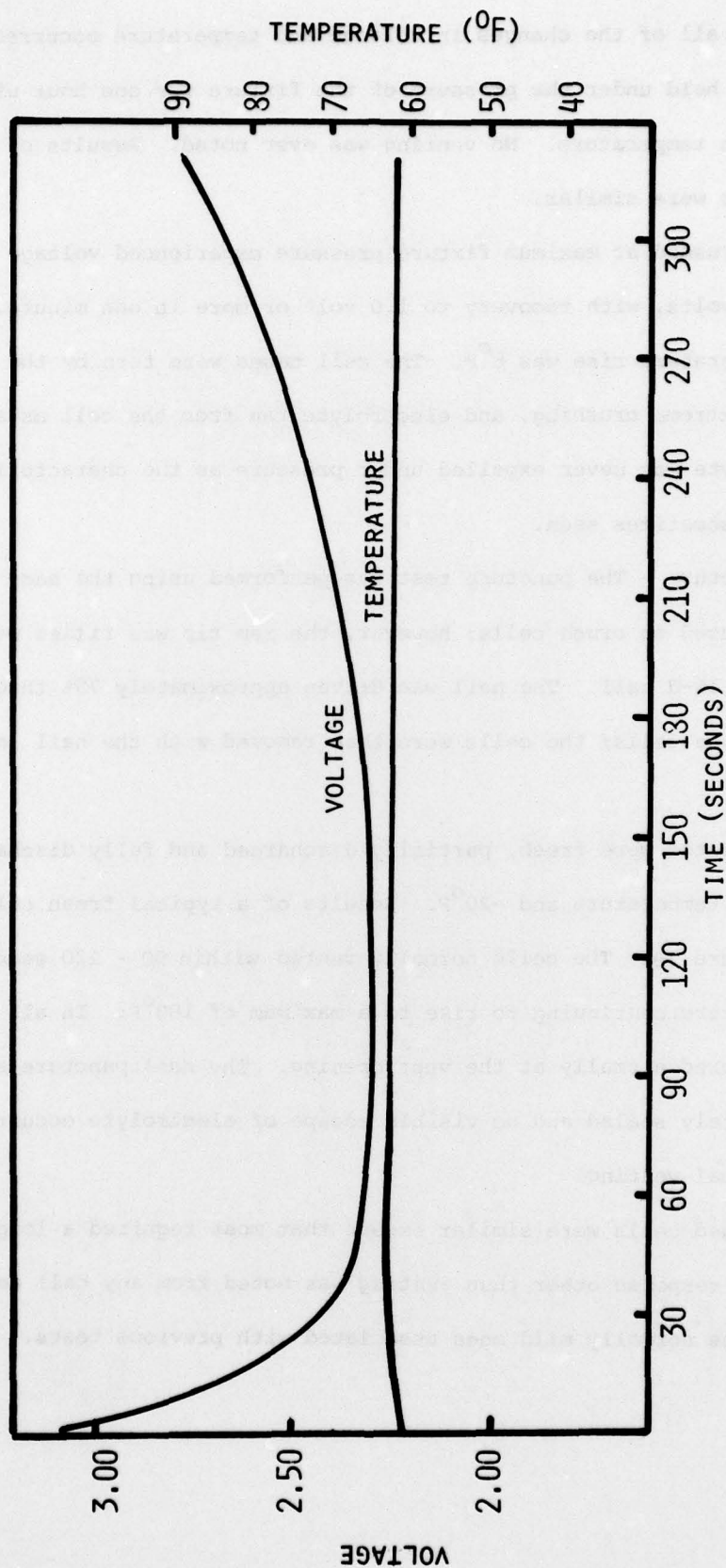
TEMPERATURE (^{0}F)

VOLTAGE

TEMPERATURE

FIGURE 38 CA/SOCL$_2$ CELL CRUSHING

TIME (SECONDS)

VOLTAGE

during which all of the changes in voltage and temperature occurred. The cell was held under the pressure of the fixture for one hour with out change in temperature. No venting was ever noted. Results of discharged cells were similar.

Cells crushed at maximum fixture pressure experienced voltage drops down to 0.6 volts, with recovery to 1.0 volt or more in one minute. The maximum temperature rise was $8^{O}F$. The cell cases were torn by the fixture during the extreme crushing, and electrolyte ran from the cell as a liquid. The electrolyte was never expelled under pressure as the characteristic white spray sometimes seen.

h) Puncture - The puncture test was performed using the same hydraulic fixture used to crush cells; however, the ram tip was fitted with a loosely held 16-d nail. The nail was driven approximately 75% through the diameter of the cells; the cells were then removed with the nail left in the cell.

Cells tested were fresh, partially discharged and fully discharged, both at room temperature and $-20^{O}F$. Results of a typical fresh cell are shown in Figure 39. The cells normally vented within 90 - 120 seconds, with temperatures continuing to rise to a maximum of $180^{O}F$. In all cases the vent occured normally at the vent opening. The nail puncture seemed to be completely sealed and no visible escape of electrolyte occurred prior to normal venting.

Discharged cells were similar except that most required a longer time to vent. No response other than venting was noted from any cell and the vents were the normally mild ones associated with previous tests.
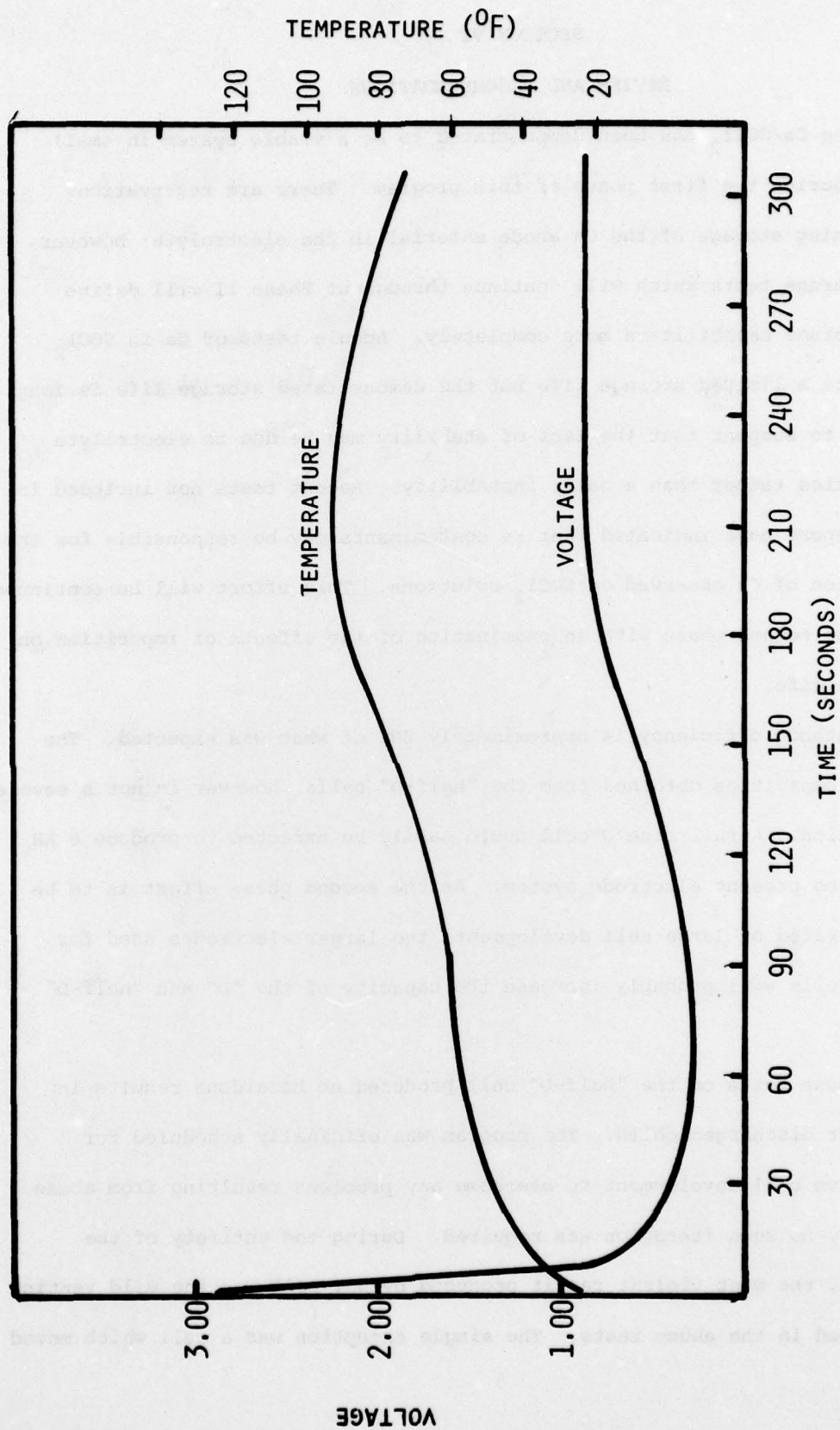
FIGURE 39 Ca/SOCl₂ CELL PUNCTURE

SECTION VI

REVIEW AND RECOMMENDATIONS

The $Ca/SOCl_2$ has been demonstrated to be a viable system in small cells during the first phase of this program. There are reservations concerning storage of the Ca anode material in the electrolyte; however, the storage tests which will continue throughout Phase II will define the storage capabilities more completely. Ampule tests of Ca in $SOCl_2$ indicate a limited storage life but the demonstrated storage life is long enough to suspect that the lack of stability may be due to electrolyte impurities rather than a basic instability. Recent tests not included in this report have indicated that Fe contaminants may be responsible for the corrosion of Ca observed on $SOCl_2$ solutions. This effort will be continued into the second phase with an examination of the effects of impurities on storage life.

Cathode efficiency is approximately 80% of what was expected. The 3.5 AH capacities obtained from the "half-D" cells, however is not a severe limitation. A full size"D"cell could easily be expected to produce 8 AH using the present electrode system. As the second phase effort is to be concentrated on large cell development, the larger electrodes used for those cells will probably increase the capacity of the "D" and "half-D" cells.

Abuse tests on the "half-D" cell produced no hazardous results in fresh or discharged cells. The program was originally scheduled for iterative cell development to overcome any problems resulting from abuse however, no such iteration was required. During the entirety of the program, the most violent result produced by any cell was the mild venting described in the abuse tests. The single exception was a cell which moved

during venting caused by short circuit early in the program. Based upon the results of the many abuse tests, and the fact that $Li/SOCl_2$ cells were made and tested at the same time, it is almost certain that the cell in question was a $Li/SOCl_2$ rather than a $Ca/SOCl_2$; a mistake which might easily have gone undetected since voltage was not monitored during the test.

The second phase of the program will be concentrated on the problems exposed in Phase I such as Fe contamination. Larger cells will be constructed in gradual stages, starting with 600 AH, 2000 AH and finally 10,000 AH, with abuse tests on 600 and 10,000 AH cells. The 2000 AH cells will be demountable for teardown and will be equipped with gas and liquid sample collection parts to be used during discharge. The 10,000 AH cells will be discharged in simple capacity tests, followed by abuse tests on fresh and discharged cells induced short circuit, reversal, puncture and incineration.